

# On the Usefulness of Imprecise Bayesianism in Chemical Kinetics

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## Abstract

Bayesian methods are growing ever more popular in chemical kinetics. The reasons for this and general challenges related to kinetic parameter estimation are shortly reviewed. Most authors content themselves with using one single (mostly uniform) prior distribution. The goal of this paper is to go into some serious issues this raises. The problems of confusing knowledge and ignorance and of reparametrisation are examined. The legitimacy of a probabilistic Ockham's razor is called into question. A synthetic example involving two reaction models was used to illustrate how merging the parameter space volume with the model accuracy into a single number might be unwise. Robust Bayesian analysis appears to be a simple and straightforward way to avoid the problems mentioned throughout this article.

**Keywords:** Imprecise probability, parameter estimation, Bayes' factors, Ockham's razor, Robust Bayesian analysis, chemical kinetics

## 1. Introduction

Chemical kinetics is the systematic study of the speed of chemical reactions [Espenson \(1995\)](#). It encompasses a wide range of fields such as combustion [Fischer and Jiang \(2015\)](#), homogeneous catalysis [Behr and Neubert \(2012\)](#), heterogeneous catalysis [Thomas and Thomas \(2014\)](#), gas-solid reactions [Favergeon et al. \(2008\)](#), and biochemistry [Cornish-Bowden and Cornish-Bowden \(2012\)](#), to name but a few. One of its main goals is to predict the concentrations of chemical species as a function of space and/or time. A reaction rate can usually be expressed as  $r = k(T) \prod_{i=1}^n C_i^{m_i}$ , where  $C_i$  is the concentration of the  $i$ -th species,  $m_i$  is the reaction order with respect to species  $i$  and  $k(T)$  is the reaction rate coefficient. The latter can often be expressed as a function of the temperature  $T$  through the Arrhenius law according to which  $k(T) = AT^n \exp(-\frac{E_a}{RT})$  with  $A$  being the pre-exponential factor,  $n$  the temperature coefficient,  $E_a$  the activation energy, and  $R = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$  the ideal gas constant. It might be necessary to consider more complex kinetic laws in specific fields such as gas-solid reactions [Favergeon et al. \(2017\)](#). In the most general case, there is a complex interaction between physics and chemistry which results in complicated systems of partial differential equations which depend on both physical and chemical unknown parameters. Chemical kinetic studies

are generally designed in such a way as to simplify the mathematical description as much as possible, so that in the ideal case it becomes a system of Ordinary Differential Equations (ODE) with respect to time (e.g. in a homogeneous batch reactor [Levenspiel \(2013\)](#) or a shock tube [Davidson and Hanson \(2003\)](#)) or with respect to one spatial dimension (as in the case of plug flow reactors [Pratt \(1979\)](#)).

At the beginning, chemical kinetics was a mostly empirical science. Modelling was limited to the estimation of kinetic parameters under conditions where only one or two reactions take place, thereby allowing for an analytical solution of the ODE system [Hughes et al. \(1936\)](#). With the increase in computational power, software have been developed to numerically solve the differential equation systems so that complex situations where hundreds or thousands of reactions compete with one another can be simulated [Lutz et al. \(1988\)](#). The systematic use of optimisation methods to estimate and adjust kinetic parameters is a rather recent development [Fischer and Riedel \(2013\)](#).

There has also been a growing realisation over the last decade that having a model which nicely fits measurements cannot be the end of the story. Authors such as Frenklach [Frenklach \(2007b\)](#) forcefully showed that there exists a great number of competing reaction mechanisms with strongly different parameter values which yet can reproduce the experimental data at hand equally well. Reliable predictions of important quantities (such as the turnover of an enzymatic reaction or the concentration of a toxic pollutant) can only be achieved if the uncertainty of the model parameters is correctly taken into account [Sheen and Wang \(2011\)](#). Like in other scientific fields, the approaches to the estimation of the parameters and their correlated uncertainties can be broadly divided into two camps, namely the frequentist and the Bayesian one, which are often (somewhat misleadingly) referred to as "determinist" and "stochastic" in the chemical kinetic community [Braman et al. \(2012b\)](#).

The aim of the present paper is to explain why the use of *precise* Bayesian methods can be very problematic in situations where only few data are available as they can blur the distinction between knowledge and ignorance and how *robust* Bayesian analysis can help practitioners avoid these difficulties. It is organised as follows. In Section 2, the different approaches are presented in the context of chemical kinetics. In Section 3, it is argued that one of the main differences between frequentism and precise

Bayesianism is the presence of an Ockham factor within the Bayes factor. In Section 4, a synthetic concentration profile was used to discriminate between two reaction models and to illustrate how a naive reliance on a single (uniform) prior can lead to misleading results. The conclusion and an outlook are given in Section 5.

## 2. Frequentist, Precise and Imprecise Bayesian Approaches

Frequentism is the view that probabilities can only be meaningfully assigned to potentially repeatable events [Mayo and Cox \(2006\)](#). In parameter estimation problems in chemical kinetics, the (most widely used) frequentist approach consists of estimating the *feasible set* of parameter values  $k$  (from a model  $M$ ) which are compatible with the  $n$  available experimental data  $e$  given their uncertainty and random fluctuations [Russi et al. \(2008\)](#); [Frenklach \(2007a\)](#); [You et al. \(2011\)](#). If we suppose that  $e$  is the realisation of the random variable vector  $X$ , for a given confidence coefficient  $\alpha$ , the feasible set is given by

$$F = \{k \mid p(|X_i(m_i(k)) - m_i(k)| \geq |e_i - m_i(k)|) \geq \alpha, i \in [1:n]\}$$

To put it in modern English, this means that the observed discrepancies between model and experiment must be small enough to be accounted for by the natural fluctuations of  $X_i$  around its expected value  $E(X_i) = m_i(k)$ . Most of the time, we suppose that the residuals follow a normal distribution (i.e.  $X_i - E(X_i) \sim N(0, \sigma_i)$ ) and are independent on one another. This naturally leads to the following definition

$$F_\epsilon = \{k \mid |m_i(k) - e_i| \leq \epsilon \sigma_i\}, i \in [1:n]$$

with  $\sigma_i$  being the standard deviation of the  $i$ -th measurement. While such a feasible set may not have good frequentist properties, it is popular among chemical kineticians because it ensures that the model is compatible with *each* experimental target [You et al. \(2011\)](#). An example of a feasible set involving three reaction coefficients of a mechanism describing the combustion of methane  $\text{CH}_4$  [Smith et al. \(Website, last access on 11.11.2014\)](#) can be seen in Figure 1. The possible values of the parameters are constrained by two experimental data sets the model has to match. As the number of experimental data increases, the feasible set becomes smaller and smaller. This, in turn, also narrows down the range of predictions of important quantities, such as heat production or the concentration of a pollutant [Russi et al. \(2010\)](#).

The likelihood of the measurements given one set of parameter values is usually computed under the (often implicit) assumption that the errors are *normally distributed* [Turányi et al. \(2012\)](#); [Sheen and Wang \(2011\)](#). It is worth noting, however, that this remains a hypothesis

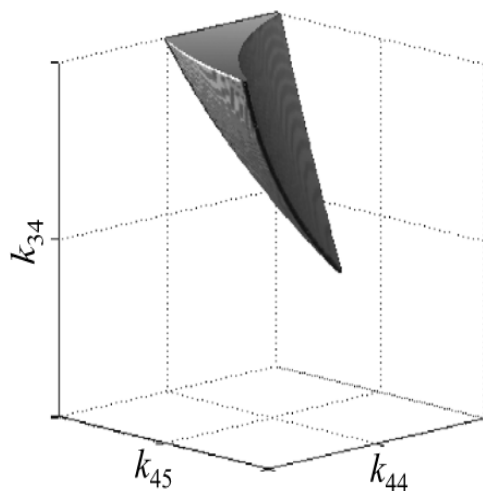


Figure 1: Example of feasible set

that is very seldom put to the test, as the experiment is generally only repeated one or two times (if at all), which is clearly not enough to validate it [Cvetanovic et al. \(1979\)](#). This is very unfortunate, as the errors stemming from not representing correctly the experimental fluctuations can have a deep impact on the parameter uncertainty [Braman et al. \(2012a\)](#). What is more, they can accumulate and strongly distort the results of the parameter estimation when hundreds of reactions and thousands of experiments are considered.

According to Bayesianism, both the measurements and the parameter values can be characterised through probability distributions [Talbot \(2005\)](#). Based on initial probabilities (the so-called *priors*), posterior probabilities are computed by using Bayes theorem upon seeing new data. In the case of continuous variables, the relationship is given by

$$f(k|e) = \frac{L(e|k)f_0(k)}{\int_{k \in K} L(e|k')f_0(k')dk'}$$

where  $f_0(k)$  is the prior probability density,  $f(k|e)$  is the posterior probability density given the measurements and  $L(e|k)$  is the likelihood. For example, the posterior probability distribution of the chemical kinetic parameters of the reaction  $\text{C}_{12}\text{H}_{26} + \frac{25}{2}\text{O}_2 \rightarrow 12\text{CO} + 13\text{H}_2\text{O}$  are shown in Figure 2. If two models  $M_1$  and  $M_2$  must be compared, the Bayes factor [Goodman \(1999\)](#) is usually employed for finding the best one. It is defined as the ratio of the total likelihoods

$$B = \frac{P(e|M_2)}{P(e|M_1)} = \frac{\int L(e|k_2, M_2)f_{2,0}(k_2|M_2)dk_2}{\int L(e|k_1, M_1)f_{1,0}(k_1|M_1)dk_1}$$

In the field of chemical kinetics, the Bayesian approach has been applied to problems as diverse as the synthesis

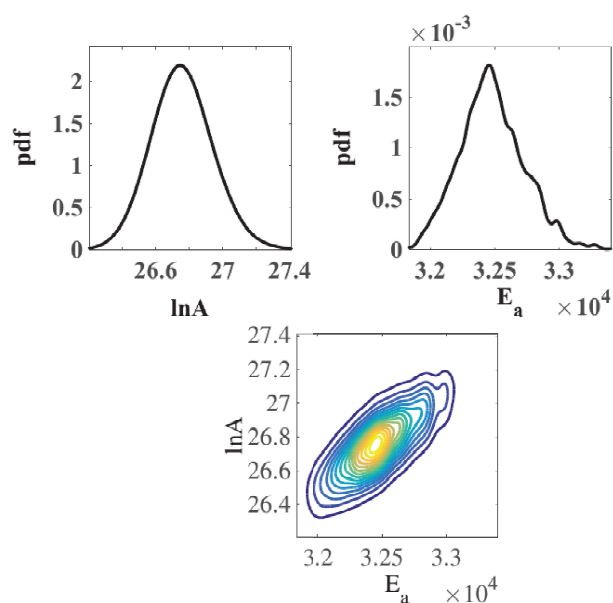


Figure 2: Posterior predictive marginal and joint distributions of Arrhenius rate parameters

of pharmaceutical products [Overstall et al. \(2018\)](#), atmospheric reactions [Miki et al. \(2012\)](#), combustion in a shock tube [Long et al. \(2014\)](#), and soot formation [Josephson et al. \(2017\)](#), to name but a few. Somewhat surprisingly, most authors [Plessis \(2013\)](#); [Urzay et al. \(2012\)](#); [Niemi and Wheeler \(2011\)](#); [Henderson et al. \(2012\)](#); [Holtzer et al. \(2001\)](#); [Josephson et al. \(2017\)](#); [Miki et al. \(2011, 2012, 2013, 2015\)](#); [Mosbach et al. \(2012, 2014\)](#); [Najm et al. \(2009\)](#); [Panesi et al. \(2011\)](#); [Prager et al. \(2013\)](#); [Sargsyan et al. \(2009\)](#); [Sondak et al. \(2017\)](#); [Wang and Sheen \(2015\)](#) do not explain why one should use Bayesian methods instead of frequentist ones in chemical kinetics. Several authors mention the higher simplicity, intuitiveness and appealing nature of the Bayesian approach [Overstall et al. \(2018\)](#); [Verheijen \(2003\)](#). According to [Sargsyan et al. \(2018\)](#), frequentism is only concerned with parameter values and ignores possible mistakes in the model assumptions. [Rodionova et al.](#) pointed out that Bayesianism readily allows researchers to divide a complex problem into a series of simpler ones [Rodionova and Pomerantsev \(2004\)](#). According to [Bell et al. \(2018\)](#), unlike frequentist methods which do not go beyond delivering a best fit with error bars, Bayesian methods determine the set of all parameter values compatible with the data. This argument is questionable, though, as there are frequentist methods (such as the feasible set approach) that have been precisely developed in order to deal with these problems in chemical kinetics [Frenklach \(2007a\)](#); [Russi et al. \(2008\)](#); [You et al. \(2011\)](#). Several authors [Braman et al. \(2013\)](#); [Duque-Bernal et al. \(2013\)](#); [Hakim et al.](#)

[\(2018\)](#) have emphasised that frequentist methods are prone to overfitting, i.e. to favouring very complex models with many parameters which perfectly match the measurements. By merging relative accuracy and simplicity into one single number (the Bayes factor), *precise* Bayesian methods avoid this problem. However, as we shall see in [Section 3](#) and [4](#), this is not necessarily always a strength as this can lead one to mistake ignorance for knowledge. Other authors mention the strongest advantage of the Bayesian framework which is its ability to integrate genuine prior information into the problem at hand [Hsu et al. \(2009\)](#); [McMullen and Jensen \(2011\)](#); [Verheijen \(2003\)](#); [Janković \(2015\)](#). For instance, while studying the homogeneous esterification of acetic acid with isoamyl alcohol, [Duque-Bernal et al.](#) used frequency data about similar esterification reactions found in the literature to define the prior distribution of the activation energy of the specific reaction they were studying [Duque-Bernal et al. \(2013\)](#). Similarly, in their study of the polymorphic transformation of L-glutamic acid crystals, [Hermanto et al.](#) used preliminary maximum likelihood estimates to inform their prior [Hermanto et al. \(2008\)](#). In such situations, traditional frequentist methods would have only considered the lower and upper bound, thereby failing to exploit important and useful prior information.

In most cases, however, the only information we have about a kinetic parameter is that it belongs to some interval [Frenklach \(2007a\)](#); [Urzay et al. \(2012\)](#); [Braman et al. \(2013\)](#); [Hsu et al. \(2009\)](#). The appropriate choice of prior probabilities in such a situation of *complete ignorance* appears to be one of the most problematic aspects of classical Bayesianism when understood as a *universal* framework [Talbott \(2005\)](#), [Staley \(2014\)](#). The *principle of indifference* (POI) stipulates, in its most general form, that one should assign an equal plausibility to each outcome of a situation if one has no grounds for preferring one of them [Norton \(2008\)](#). Applied to *point probabilities*, it naturally leads to a uniform distribution [Norton \(2008\)](#). This, however, blurs the fundamental distinction between warranted knowledge and ignorance. If we know absolutely nothing about a coin, we cannot assume that the probability of its landing odds is 0.5 as if we knew through careful measurements that it is perfectly poised [Walley \(2000\)](#); [Salmon \(1967\)](#). What is more, let us suppose that the only thing we know about a pre-exponential factor  $A$  in chemical kinetics is that it belongs to the interval  $[10^{10}; 10^{16}]$ . A straightforward application of the principle of indifference leads to  $p_1 = p(A \in [10^{12}; 10^{14}]) = (10^{14} - 10^{12}) / (10^{16} - 10^{10}) = 0.0099$ . Now, if we are completely ignorant about  $A$ , we are also ignorant about  $\log_{10}(A)$ . However applying the principle of indifference to it leads to  $p_2 = p(\log_{10}(A) \in [12; 14]) = p(A \in [10^{12}; 10^{14}]) = (14 - 12) / (16 - 10) = 0.33333 = 33.67p_1$ . The consideration of other reparametrisations can lead to an endless number of such paradoxes [Norton \(2008\)](#). According to [Norton \(2008\)](#), this demonstrates the

fact that a state of complete ignorance cannot be represented through a *single* probability distribution. This issue has led Jeffreys to develop a prior which is insensitive to the parametrisation of the problem [Jeffreys \(1946\)](#). While Jeffreys' prior avoids the charge of arbitrariness, it cannot be considered a genuine representation of ignorance as it (often strongly) favours some parameter values over others [Norton \(2008\)](#); [Kass and Wasserman \(1996\)](#). The impossibility of representing a state of complete ignorance through a single probability distribution is thus one of the main shortcomings of *precise* Bayesianism. This is where imprecise probability (forming the basis of robust Bayesianism) can be fruitfully employed [Berger \(1990\)](#). The probability of an event (such as that of a coin landing odds) is no longer always represented by a single value but by a probability interval (which would be  $[0;1]$  in the case of complete ignorance) [Walley \(2000\)](#). The prior uncertainty about the values of a parameter is no longer described through a single distribution but through a family of distributions which must be large enough to represent ignorance [Hall \(2006\)](#). The difference between the posteriors corresponds to the imprecision which can be reduced by increasing the size of the experimental data set.

Whilst robust Bayesian methods are now considered a respectable approach in statistics [Berger et al. \(1994\)](#); [Radanovic and Faltings \(2013\)](#), they are very rarely used in chemical kinetic studies, although a few authors are aware of the fact that the posterior can be very sensitive to the prior [Braman et al. \(2013\)](#); [Galagali \(2016\)](#). Instead, almost all chemical kineticists rely on a single prior which is most often uniform [Plessis \(2013\)](#); [Urzay et al. \(2012\)](#); [Bell et al. \(2018\)](#); [Braman et al. \(2012b\)](#); [Hakim et al. \(2018\)](#); [Hsu et al. \(2009\)](#); [Josephson et al. \(2017\)](#); [Miki et al. \(2011, 2012, 2013, 2015\)](#); [Panesi et al. \(2011\)](#); [Najm et al. \(2009\)](#); [Prager et al. \(2013\)](#); [Sargsyan et al. \(2009\)](#). For their study, Emerson Holtzer et al. used bounded Gaussian priors they set up arbitrarily [Holtzer et al. \(2001\)](#). Braman et al. systematically used both a uniform and a normally distributed prior for their estimation of the chemical kinetic parameters of syngas combustion [Braman et al. \(2013\)](#). In that respect, they have implicitly embraced part of the philosophy of imprecise probability as the total information about the problem is no longer contained in a single probability distribution. Nevertheless, a real robust Bayesian analysis would have necessitated a much greater number of priors [Berger et al. \(1994\)](#). Likewise, in his work devoted to the Bayesian inference of chemical reaction networks [Galagali \(2016\)](#), Galagali recognised that different priors (uniform, normal, exponential) might be equally justifiable and reasonable, but he limited himself to three point-mass mixture priors, which is clearly not enough to determine the whole influence that the choice of the prior can have on the posterior. To conclude, we can fairly say that the large majority of chemical kineticists applying Bayesian

methods to their parameter estimation problems only use a single uniform prior distribution and that in the few cases where researchers wonder about the impact of the prior on the posterior, they only consider one or two other priors.

### 3. Ockham Factors: A Major Difference Between Frequentism and Precise Bayesianism

Let us suppose that we are comparing two models  $M_1$  and  $M_2$  which aim at accounting for the same experimental data  $E$ .  $k_1$  and  $k_2$  are their parameter vectors. The volumes of their parameter spaces are  $V_{M1}$  and  $V_{M2}$ , respectively and we further assume that their likelihoods are characterised by two peaks occupying the volumes  $V_{PM1}$  and  $V_{PM2}$ , respectively. The Bayes' factor  $B$  can be expressed as

$$B = \frac{L(E|M_2)}{L(E|M_1)} = \frac{\int_{k_2} L(E, k_2, M_2) f_{2,0}(k_2|M_2) dk_2}{\int_{k_1} L(E, k_1, M_1) f_{1,0}(k_1|M_1) dk_1}$$

$$B = \frac{L_{\max}(E|k_2)}{L_{\max}(E|k_1)} \frac{V_{PM2}}{V_{PM1}} \frac{V_{M1}}{V_{M2}} = F Q_p O$$

if we apply the principle of indifference to  $f_{1,0}(k_1|M_1)$  and  $f_{2,0}(k_2|M_2)$ .  $F$  is the ratio of the maximum likelihoods of the two models. It is the quantity that often plays the most important role in frequentist comparisons of models. This comparison of the maximum likelihoods is the approach that has been traditionally used by chemical kinetics trying to discriminate between two competing reaction mechanisms on the basis of experimental data ([Hunter and Reiner, 1965](#); [Reilly, 1970](#)), often indirectly through a comparison of the optimal values of the chi-squared distance ([Wagner et al., 2016](#)) and sometimes more incorrectly of the least-squared distance ([Tan et al., 1988](#)). The main difference between the *precise* Bayesian approach and the frequentist approach consists of the Ockham factor  $O = (\frac{V_{M2}}{V_{M1}})^{-1}$ . Following the philosophical principle of Ockham's razor, it penalises the model that is the most complex, whereby complexity is defined as the total volume of the parameter space. This reasoning can be found in an article written by Braman et al. about the quantification of uncertainty in syngas chemistry models [Braman et al. \(2012a\)](#). Strongly relying on the work of objective Bayesian physicist E.T. Jaynes [Jaynes and Bretthorst \(2003\)](#), the authors considered that a uniform prior is an appropriate representation of ignorance (even though they recognise that the posterior can be very sensitive to the choice of the prior) and that this entails Ockham's razor.

However, if the principle of indifference is not correct, that demonstration is invalid.

It is trivial to see how  $O$  is highly dependent upon the parameter representation. Let us consider, for example, that  $p_1 \in [1; 1E + 10]$  and  $p_2 \in [1; 1E + 100]$  while  $F = Q_p = 1$ . If we directly apply the principle of indifference, we find

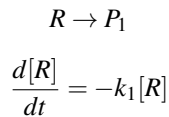


that  $O_p \approx 1E - 90$ , which would mean that we know with almost absolute certainty that  $M_1$  is false. If, however, we apply the POI to  $\log_{10}(p_1)$  and  $\log_{10}(p_2)$ , we find that  $O_{\ln(p)} \approx 0.091$ . And if we apply the POI to  $p_1^{-1}$  and  $p_2^{-1}$ , we find that  $O_{p^{-1}} \approx 1$ . It is important to keep in mind that if we are totally ignorant about the distribution of the values of  $p_i$ , we should logically be equally ignorant about the values of  $\log_{10}(p_i)$  and  $p_i^{-1}$ . According to Wolpert (1995), this Bayesian demonstration of Ockham's razor fails because  $O$  depends on the choice of the variable. The only way to make the ratio of the posteriors independent on the parametrisation would be to always select the following prior probabilities for the models:  $p(M_1) = V_{M_1}$  and  $p(M_2) = V_{M_2}$ , which would effectively shave away the razor.

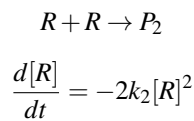
#### 4. How Not to Mix Ignorance and Knowledge

To see how this problem can negatively affect the work of chemical kineticists, a synthetic experimental data set was used to discriminate between two models. Let us consider an experimental profile that we want to simulate with two models  $M_1$  and  $M_2$ . The standard deviation of any measurement  $e_i$  is given by  $\sigma_i = 0.065e_i$ . Let us further assume that there are only two reaction models which could account for the data

- $M_1$  : An isomerisation towards product  $P_1$ :



- $M_2$  : A recombination towards product  $P_2$ :



and that products  $P_1$  and  $P_2$  cannot be detected. In each case, the ordinary differential equation given above must be solved, given the initial condition  $[R]_0 = 1200 \text{ mol/m}^3$ . Since it involves the rate coefficient  $k_i$ , the computed temporal evolution of  $R$  (and thus the likelihood as well) are also bound to depend on it.

For theoretical and empirical reasons, we know the lower and upper bound of each kinetic coefficient while lacking any information about the distribution of the possible values. While an analogy with other reactions allows us to set narrow bounds for  $k_1$  ( $k_1 \in [2; 2E + 3]s^{-1}$ ), the uncertainty concerning  $k_2$  is far larger in that  $k_2 \in [5E + 04; 5E + 09] \text{ mol.cm}^{-3}.s^{-1}$ . We want to determine whether or not the data allow us to identify which of the two models is the most plausible.

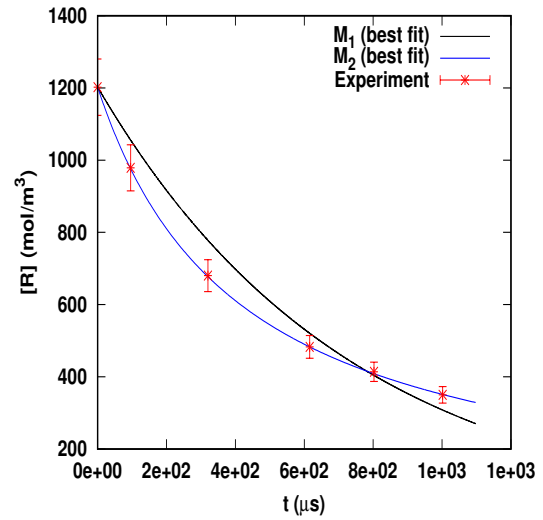


Figure 3: Optimised profiles of  $R$ .

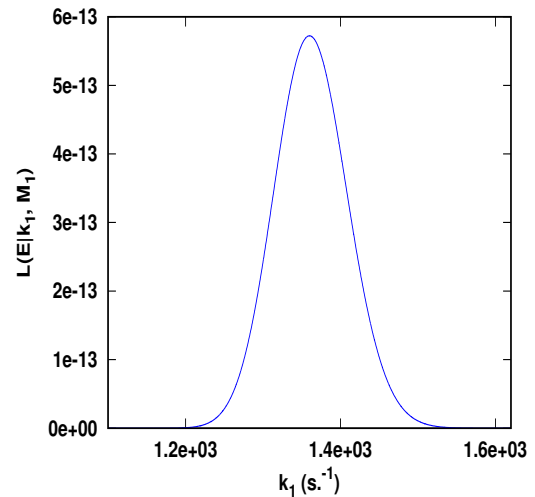


Figure 4: Likelihood ( $M_1$ )

##### 4.1. Frequentist Approach

The optimal curves obtained via the maximum likelihood method are contrasted with the measurements in Figure 3. The likelihood function of  $M_1$  and  $M_2$  can be seen in Figure 4 and 5, respectively.

For  $\varepsilon = 2$  and  $F_\varepsilon = \{k \mid |m_i(k) - e_i| \leq \varepsilon \sigma_i\}$ ,  $i \in [1; n]$ , the feasible set approach leads one to discard  $M_1$  as its feasible set is empty. The feasible set of  $M_2$  is given by  $k_2 \in [8.51E + 05; 1.22E + 06] \text{ mol.cm}^{-3}.s^{-1}$ . The ratio between the maximum likelihood of  $M_2$  and  $M_1$  is  $F = 322.91$ .

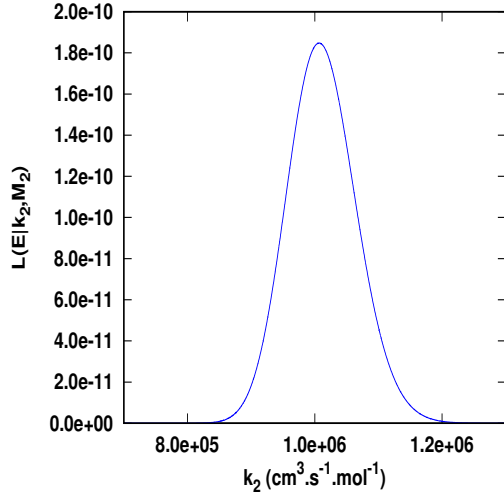


Figure 5: Likelihood ( $M_2$ )

#### 4.2. Precise Bayesian Approach

Applying the principle of indifference directly to  $k_1$  and  $k_2$  leads to the following uniform priors:  $P(k_1|M_1) = 1/(2^3 - 2) = 0.00050$  and  $P(k_2|M_2) = 1/(5^9 - 5^4) = 2^{-10}$ . After having computed the likelihood function, we can compute the Bayes factor  $B$  (see Section 3).

We find that  $B_k = 0.312$ , which means that we ought to privilege  $M_1$  over  $M_2$ , even though the predictions of  $M_1$  are farther from the measurements, and crucially, even though  $M_1$  (unlike  $M_2$ ) fails to reproduce the shape of the experimental profile. This is an example of Lindley's paradox where frequentist and Bayesian methods lead to conflicting results [Robert \(2014\)](#). This is caused by the fact that the knowledge consisting of the experimental data (which boils down to aleatory uncertainty) was illegitimately mixed up with our ignorance over the parameter values (epistemic uncertainty). Several authors have pointed out that while aleatory uncertainty can often be represented through a single probability distribution (provided there is enough data), epistemic ignorance cannot be treated in this manner [He et al. \(2015\)](#); [Abdallah et al. \(2013\)](#); [Bae et al. \(2004\)](#); [Mathon et al. \(2010\)](#).

#### 4.3. Robust Bayesian Approach

It is precisely in such ambiguous situations that imprecise probabilities can prove extremely fruitful [Walley \(2000\)](#). Instead of only considering a single prior probability density, we will now consider six of them, namely  $f_k, f_x, f_l, f_y, f_z,$  and  $f_w$ . They were obtained by reparametrising the problem and attributing a flat prior to the new parameter, following the same logics as in Sections 2 and 3. These new variables are such that  $x = 1/k, l = \log_{10}(k), y = 1/\log_{10}(k), z = k^{0.25},$  and  $w = k^2$ . Of course, more sophisticated priors

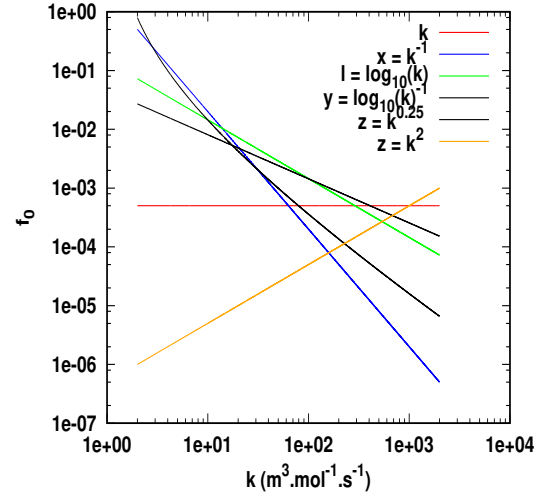


Figure 6: Prior distributions for  $p_1$  ( $M_1$ )

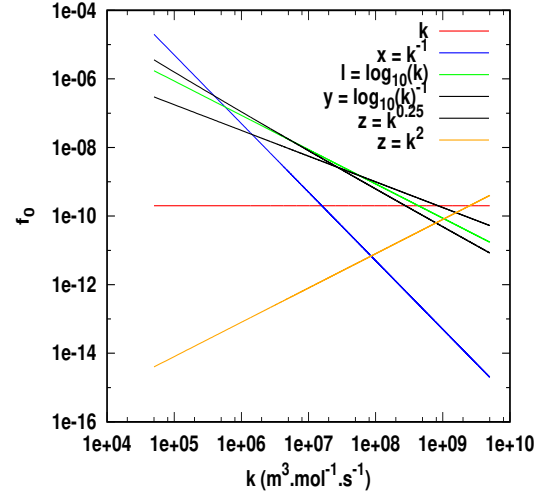


Figure 7: Prior distributions for  $p_2$  ( $M_2$ )

can be used or built up in the framework of robust Bayesian analysis [Ferson et al. \(2015\)](#); [Berger et al. \(1994\)](#). The main advantage of the priors defined in this section is that they are all uniform with respect to one variable and are equally justifiable, *if we adopt a precise Bayesian framework*<sup>1</sup>, in that being totally ignorant about the values of  $k$  logically entails being also totally ignorant about the values of  $x, l, y, z,$  and  $w$  [Norton \(2008\)](#). The priors for  $M_1$  and  $M_2$  can be seen in Figure 6 and 7, respectively. The Bayes factor was recomputed along with the Ockham factor. The results can be seen in Table 1. It is striking that the values of the Bayes' factor are strongly dependent on the prior. This is

1. From an imprecise Bayesian standpoint, none of the priors alone can represent ignorance. Only all priors taken together are an adequate representation of our lack of knowledge.

Variable	O	B
$k$	4.00E-07	3.12E-01
$x = 1/k$	2.50E+04	1.67E+04
$l = \log_{10}(k)$	6.00E-01	3.29E+02
$y = 1/\log_{10}(k)$	2.75E+01	3.74E+03
$z = k^{0.25}$	2.19E-02	7.08E+01
$w = k^2$	1.60E-13	1.98E-04

Table 1: Dependency of  $O$  and  $B$  on the prior

due to the Ockham factor  $O$  that heavily penalises  $M_2$  in the case of  $k$  and  $w = k^2$  whereas it favours it in the case of  $x = 1/k$  and  $y = 1/\log_{10}(k)$ . Interestingly,  $l = \log_{10}(k)$  leads to the value of  $B_l = 3.29E + 02$  that is the closest to the maximum likelihood ratio  $F = 322.91$ , which is a purely experimental quantity (if we know the physical distribution of the measurement uncertainty). Nevertheless, there is no reason to suppose that priors based on  $\log_{10}(k)$  will always have that desirable quality.

#### 4.4. Discussion

The simplicity of this example allows one to rapidly visualise, analyse and understand the nature of the problem. The consequences of mixing knowledge and ignorance are, however, often not so easy to recognise (see Norton (2010); Benetreau-Dupin (2015)). Clearly, an experienced Bayesian statistician would not commit the fallacy described in 4.2. Nevertheless, as we saw in Section 2, most chemical kineticists who resort to Bayesian methods only use one single uniform prior Plessis (2013); Urzay et al. (2012); Bell et al. (2018); Braman et al. (2012b); Hakim et al. (2018); Hsu et al. (2009); Josephson et al. (2017); Miki et al. (2011, 2012, 2013, 2015); Panesi et al. (2011); Najm et al. (2009); Prager et al. (2013); Sargsyan et al. (2009), and some of them even state that this is the only logical choice if everything we know about a parameter is its lower and upper bound Hsu et al. (2009). Prior sensitivity analyses are very rare and limited to the use of one or two additional priors Galagali (2016); Braman et al. (2012b). As such, it is unclear whether the results in all these works only reflect the experimental data or both the data and the prior.

In their work about the reaction pathways underlying the electrochemical reduction of nitrate on tin, Katsounaros et al. described the Bayes factor as the pure impact of the data on the model relative plausibility Katsounaros et al. (2012), like many other authors in the general field of parameter estimation Alatri (1999); Rouder et al. (2018); Morey and Rouder (2011). In the presence of a prior distribution based on empirical information, Bayes factors can indeed be a very useful tool to discriminate between models which is far superior to the traditional  $p$ -value tests Goodman (1999). However, in the case of the two reaction models we just considered here (see Fig. 3), it is clearly wrong to say that

it is the *data themselves* which disfavour  $M_2$  ( $B_k = 0.312$ ). It would, on the contrary, be more appropriate to say that our decision to try to represent our ignorance through a flat prior on  $k$  *smothered* the experimental information at our disposal. In their work on the Bayesian analysis of syngas chemistry models, Braman et al. mentioned and emphasised the danger of overfitting highly complex models and argued that the closeness of an optimised model to all measurements cannot be the sole arbiter of its worth and truth Braman et al. (2013). They went on to praise the ability of *precise* Bayesianism to deliver us a *single number* combining the lack of complexity of a model and its ability to reproduce experimental data. However, the inability of precise Bayesianism to represent true ignorance might appear to be too high a price to pay for that Salmon (1967).

Even if we do not equate ignorance with uniform probability, there are other reasons to strongly favour simple models over complex ones. Kelly argued that systematically choosing the simpler of two equally accurate models maximises our convergence rate to the true model, regardless of whether it is simple or complex Kelly (2007). While overfitting complicated chemical models should always be avoided, the simplicity of a model is not necessarily related to its plausibility Sober (2015).

## 5. Conclusion and Outlook

Chemical kinetics determines many processes and phenomena that play a crucial role in the modern world, such as the combustion of fossil and renewable fuels Fischer and Jiang (2014), catalytic reforming Dou et al. (2010), the reduction of pollutant emissions from car and truck engines Kandyas et al. (1999), the growth of multicellular cancer Bajzer et al. (1997), the depletion of ozone in the stratosphere Solomon et al. (1986), and other atmospheric reactions influencing global warming Sulbaek Andersen et al. (2011). As a consequence, a good knowledge of chemical kinetic parameter uncertainty might prove crucial to face the challenges of the modern world.

Over the last decades, an increasing number of authors have applied both frequentist and Bayesian methods to chemical kinetic parameter estimation (including optimal design) Frenklach et al. (2004); Wang and Sheen (2015). The main advantage of the Bayesian approach is its ability to take into account genuine prior information (such as a frequency distribution of the rate coefficients of reactions of a certain type) and to provide decision makers with quantities that are intuitively much more appealing than their frequentist counterparts (compare, for instance, the frequentist and Bayesian notion of confidence interval). However, in situations where prior experimental knowledge is limited or non-existent, the problem cannot be described through a single prior probability distribution. Bayesian robust analy-

sis, the systematic study of the influence of the choice of the prior on the posterior variables of interest, has been applied to a large number of topics such as climatology [Tomassini et al. \(2007\)](#), the monitoring of clinical trials [Greenhouse and Wasserman \(1995\)](#), pipeline failure [Cagno et al. \(2000\)](#), and accident proneness [Insua et al. \(1999\)](#), to name but a few. However, the large majority of chemical kineticists resorting to Bayesian methods only use one single (mostly uniform) prior distribution. In Section 2 and 3, it was shown that in the absence of prior information, relying on a single uniform prior blurs the distinction between knowledge and ignorance. A simple example of chemical kinetics involving the comparison of two reactions to account for the same experimental profile was drawn upon to illustrate how the complexity of a model (i.e. the volume of its parameter space) and its accuracy (i.e. the closeness of its predictions to the measurements) are two irreducible quantities that were artificially merged into a single number because of the use of a uniform prior. There are many other ways in which the posterior might be strongly influenced by the choice of the prior. When considering the probability that an explosion might occur or that a toxic chemical might be formed, it is vital to make sure it is the experimental data that are speaking and not the prior. The purpose of this article was to draw attention to this fact and to encourage chemical kineticists employing Bayesian methods to systematically determine the sensitivity of their results to the prior.

An important question needs now to be addressed. It is well known that the influence of the prior is bound to decrease as the number of experimental data rises. This is commonly referred to as *washing out the priors* [Nola and Irzik \(2005\)](#). Is it not reasonable to expect that, from a given number of measurements, the choice of the prior will no longer matter anyway? If every new measured variable were equally sensitive to every reaction, this is something we could feel relatively confident about. Unfortunately, we know that this is rarely the case in chemical kinetics. For instance, if we consider the combustion of methane  $\text{CH}_4$ , carbon monoxide  $\text{CO}$  and hydrogen  $\text{H}_2$ , the reaction  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$  will almost always play a very significant role whereas the reaction  $\text{HO}_2 + \text{CO} \rightarrow \text{OH} + \text{CO}_2$  can be neglected for most macroscopic experimental targets such as ignition delay times and laminar flame speeds involving either  $\text{CH}_4$  or  $\text{CO}$  as fuel [Peters and Rogg \(1993\)](#) so that only few experimental data will constrain its values. And yet, it can play an important role in the combustion of bio-syngas ( $\text{CO} - \text{CO}_2 - \text{CH}_4 - \text{H}_2$  mixtures) at high pressures and middle temperatures [Fischer and Jiang \(2014\)](#) so that accurate values of its kinetic parameters would be required for, say, minimising the formation of pollutants in a combustor under these conditions. As a consequence, even in cases where we have a lot of measurements at our disposal, the choice of the prior will still have a strong

influence on the parameters most measured variables are not sensitive to so that it cannot be "washed away" easily. A systematic application of robust Bayesian analysis to chemical kinetic problems appears thus to be always advisable. There is also a need for chemical kinetic studies where both frequentist and Bayesian methods are applied to the *same* problem in order to see the practical differences caused by the choice of the fundamental framework. To the best of the author's knowledge, no such work can be found in the literature about chemical kinetics.

The results of such studies would give us important insights into how to optimally represent the uncertainty of chemical kinetic parameters in a way that would make them safer for decision makers to rely on.

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