Precise and imprecise Bayesianism applied to gas-solid reactions

Marc Fischer[1]

Loïc Favergeon[1]

[1]Laboratoire Georges Friedel (CNRS UMR 5307), Centre SPIN, Mines Saint-Etienne, France

ABSTRACT

Gas–solid reactions play a crucial role in sustainability, yet very few studies have focused on the uncertainty of their chemical kinetic parameters and its propagation. In this pioneering work, based on a numerically generated synthetic dataset of conversion profiles, we address the uncertainty arising from variations in powder particle size between any two small powder samples, which impacts experimental conversion profiles. This variation is assumed to follow a log-normal distribution and is propagated into the uncertainty of the activation energy, which subsequently affects the uncertainty of the delay time at which the chemical conversion reaches a desired value under other conditions. Both precise and imprecise Bayesian approaches were compared. The results indicate that precise Bayesian methods struggle to differentiate effectively between varying levels of knowledge. In contrast, the imprecise Bayesian method based on a set of truncated normal distributions proved efficient and significantly more useful than the one based on uniform priors for this purpose. Finally, we provide suggestions on how to apply this methodology to more realistic settings.

Keywords. imprecise probability, chemical kinetics, gas-solid reactions, priors

1. INTRODUCTION

Non-catalytic gas-solid reactions play a pivotal role in advancing sustainable technologies [18], particularly in mitigating greenhouse gas emissions and addressing global environmental challenges. Gas-solid reactions offer robust, scalable, and cost-effective solutions that directly contribute to carbon dioxide (CO_2) reduction and other environmental benefits [29].

A prominent example is the carbonation of calcium oxide (CaO), where CO_2 reacts with CaO to form calcium carbonate ($CaCO_3$) [2]. This reaction underpins carbon capture and storage (CCS) strategies, enabling the sequestration of CO_2 from industrial emissions in a stable, solid form [23, 24]. Similarly, the reduction of iron oxides using hydrogen (H_2) provides a pathway to decarbonise steel production by minimising the reliance on coke, a major source of carbon emissions [11].

Another significant application is the mineralisation of magnesium oxide (MgO) to produce magnesium carbonate ($MgCO_3$). This process facilitates the long-term storage of CO_2 in basalt formations, contributing to the direct air capture (DAC) of atmospheric CO_2 [25].

Last but not least, thermochemical energy storage through reversible gas-solid reactions, such as the cyclical reduction and oxydation of metal oxides / metals, offers an efficient pathway for harnessing and storing solar energy for on-demand use [20].

Collectively, these non-catalytic gas-solid reactions highlight their potential for sustainable development. By reducing CO_2 emissions, mitigating air pollutants, and fostering renewable energy systems, they represent a vital component in achieving a low-carbon future.

In spite of their importance, only a few works have been devoted to uncertainty propagation in this field, and the chemical kinetic models employed in the field of gas-solid reactions depend on crucial hypotheses that are rarely verified, thereby undermining confidence in the model's results [6, 16]. The lack of commonly adopted, reliable methodologies can lead to considerable discrepancies among chemical kinetic models and parameter values obtained by different research teams, as observed in the case of iron ore reduction by hydrogen for industrial production [11]. In addition to the absence of generally accepted, trustworthy chemical kinetic modelling strategies for gas-solid reactions, the impact of the lack of repeatability in experimental results on chemical paramer estimation has been scarcely studied. With only a few exceptions [13], Bayesian techniques for propagating experimental uncertainties into model uncertainties are extremely rare and typically rely on a single prior probability distribution, assumed to represent our initial uncertainty about the chemical kinetic parameter values. However, several authors have highlighted that relying on a single prior probability distribution can be deeply problematic, particularly when only limited empirical data are available, as it obscures the critical distinction between knowledge and ignorance [8, 10, 14, 28].

In this study, we seek to apply and compare a precise and an imprecise Bayesian approach (utilising multiple priors) for a gas-solid chemical kinetic problem involving

a realistic model and numerically generated temporal profiles (of the chemical conversion degree) mimicking real-world experiments, where the source of uncertainty arises from the random variation in the particle size of each powder sample used in experiments. In Section 2, we introduce our chemical scenario alongside the precise and imprecise Bayesian methods that will be compared. In Section 3, we present and critically analyse our results, before concluding in Section 4.

2. SCENARIO AND METHODOLOGY

2.1. Scenario. We consider the following reaction involving powders with spherical particles, an instantaneous nucleation, inward anisotropic growth, and a rate-limiting step located at the inner interface, commonly referred to as model R_3 in the heterogeneous kinetic literature [16, 27]:

$$A(s) + B(g) \rightarrow C(s) + D(g). \tag{1}$$
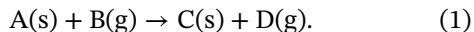
We suppose that the molar volume of the solid species A(s) is given by $V_{mA} = 1.3 \times 10^{-4}$ m³/mol and that it is equal to the molar volume of the solid species C(s), V_{mC}. For a powder consisting only of particles with a radius r_0, if we consider an apparatus such as a thermobalance with adapted experimental conditions where the chemical reaction has no significant influence on the partial pressure and temperature fields (which are assumed to be known and to be spatially homogeneous within and around the crucible holding the reactive powder and where a small powder quantity such as 10 mg is used, so that matter and heat diffusion processes are nearly instantaneous in comparison to chemical processes), the temporal profile of the conversion degree is governed by Differential Equation 2 involving the reaction rate:

$$\frac{d\alpha}{dt} = \phi(T)\frac{3V_{mA}}{r_0}(1-\alpha)^{2/3}. \tag{2}$$

By integration under isothermal conditions (i.e. $T = $ Cst), we obtain Equation 3:

$$\alpha(t) = 1 - \left(1 - \frac{\phi V_{mA}}{r_0}t\right)^3. \tag{3}$$

Here, $\alpha(t), t \geq 0$, only takes values between 0 and 1, where 0 means that the reaction has not yet begun, and 1 means that the reaction has ended and the solid reactant A(s) has been completely converted into the product C(s). The function $\alpha(t)$ is monotonically increasing and cannot decrease. The term $\phi(T)$ is the areic reactivity of growth (in mol/m²/s), which is (under our scenario) a function of temperature, as described by Equation 4:

$$\phi(T) = A \times e^{-\frac{Ea}{R \times (T + 273.15)}}. \tag{4}$$

Here, $A = A_{\text{true}} = 4.38 \times 10^{-3}$ mol/(m² · s) is the pre-exponential factor, and $E_a = E_{a,true} = 1.54 \times 10^4$ J/mol is
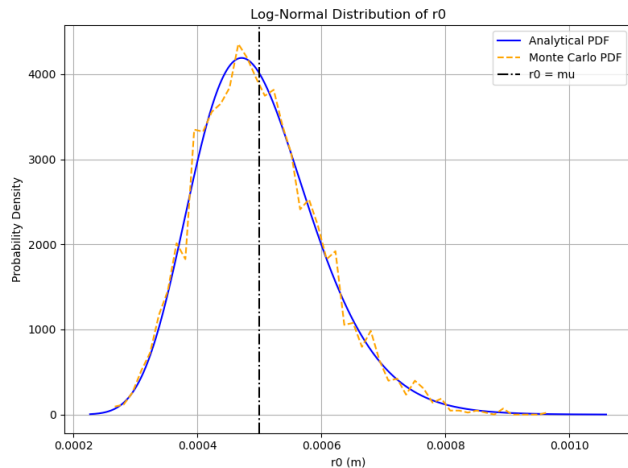

Figure 1. *Log-Normal Distribution of r_0: Analytical vs Monte Carlo Simulation.*

the apparent activation energy and T is the temperature in °C. We assume that each powder sample of 10 mg contains spherical particles with approximately the same radius, r_0, such that Equations 2 is valid (as well as 3 when T stays constant).

However, we also assume that r_0 is a random variable that varies between powder samples used in the experiments, following a log-normal distribution: $r_0 \sim$ logNormal(μ, σ), with $\mu = E(r_0) = 5 \times 10^{-4}$ m and $\sigma = std(r_0) = 0.20 \times \mu$ that are known to us through a large number of granulometric measurements. Based on A_{true} and $E_{a,true}$, we generated a series of n_{exp} **isothermal virtual experiments** conducted at $T = 30$°C whereby the radius of the powder sample r_0 varied randomly from experiment to experiment according to the log-normal distribution mentioned just above.

For the parameter estimation (inverse problem) we want to consider, we then suppose we are in the situation of an engineer who knows A_{true} while only knowing that $E_{a,true} \in [1 \times 10^4; 2 \times 10^4]$ J/mol, and our objective is to estimate it through the n_{exp} isothermal experiments we just explicated.

The log-normal distribution of r_0 can be visualised in Figure 1 and ten profiles of $\alpha(t)$ (at $T = 30$°C) corresponding to ten random values of r_0 are shown in Figure 2.

We then seek to compute the *best prediction* of the delay time t_d such that $\alpha(t_d) = 0.80$ under the following conditions:

- The temperature is not constant but increases from 30°C to 300°C at a heating rate of 1°C/min, such that

$$T(t) = \min(30 + \frac{1}{60} \cdot t, 300), \quad t > 0.$$

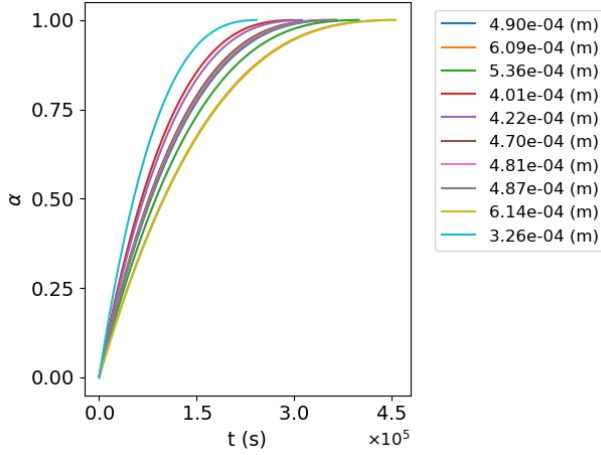- The powder consists of particles with a fixed size

Figure 2. $\alpha(t)$-profiles corresponding to ten (virtual) experimental trials alongside the corresponding values of r_0.

$$r_{0,\text{desired}} = 1 \times 10^{-4} \text{ m}.$$

This could, for example, be useful to stop the reaction once this conversion degree has been reached.

We want then to consider several values of n_{exp} (the number of isothermal experiments) corresponding to several levels of knowledge and what impact this has on the likely values of t_d in a precise and imprecise Bayesian framework.

2.2. Precise Bayesianism. As explained in detail in Appendix A, under isothermal conditions, if we consider the relationship for another delay time t_{50} when $\alpha(t_{50}) = 0.5$, it is given by Equation 5:

$$\phi = \frac{r_0(1 - 0.5^{1/3})}{V_{mA} \cdot t_{50}}. \tag{5}$$

Here, ϕ is the exact areic reactivity of growth we would obtain if the approximate radius of all powder sample particles used in the thermobalance r_0 were perfectly known. Since we are unable to measure r_0 before each experiment without destroying the 10 mg powder sample, we assume that $\hat{r_0} = \mu$ represents the estimated radius of all powder samples. The estimated value of ϕ, denoted as $\hat{\phi}$, is then given by:

$$\hat{\phi} = \frac{\mu(1 - 0.5^{1/3})}{V_{mA} \cdot t_{50}}. \tag{6}$$

This leads to the relationship in Equation 7:

$$r_0 = \frac{\phi \cdot \mu}{\hat{\phi}}. \tag{7}$$

Using this and knowing that r_0 is log-normally distributed, we derive Equation 8 for the conditional proba-

bility density:

$$f(\hat{\phi} \mid \phi) = \frac{1}{r_0 \cdot \sigma_{\log}\sqrt{2\pi}} \exp\left(-\frac{(\ln(r_0) - \mu_{\log})^2}{2\sigma_{\log}^2}\right) \cdot \frac{\phi \cdot \mu}{\hat{\phi}^2}, \tag{8}$$

where $r_0 = \phi \cdot \mu/\hat{\phi}$.

Based on the Arrhenius equation for ϕ (see Equation 4), the conditional probability density of $\hat{\phi}$ given E_a is given by Equation 9:

$$f(\hat{\phi} \mid E_a) = f_{r_0}\left(\frac{\phi(E_a) \cdot \mu}{\hat{\phi}}\right) \tag{9}$$

$$\cdot \frac{\phi(E_a) \cdot \mu}{\hat{\phi}^2} \tag{10}$$

where $f_{r_0}(r)$ is the log-normal density of r_0:

$$f_{r_0}(r) = \frac{1}{r \cdot \sigma_{\log}\sqrt{2\pi}} \exp\left(-\frac{(\ln(r) - \mu_{\log})^2}{2\sigma_{\log}^2}\right), \tag{11}$$

with the log-normal parameters:

$$\sigma_{\log} = \sqrt{\ln\left(1 + \left(\frac{\sigma}{\mu}\right)^2\right)}, \tag{12}$$

$$\mu_{\log} = \ln(\mu) - \frac{\sigma_{\log}^2}{2}. \tag{13}$$

Now, if we consider a set of n_{exp} experiments, and neglect random fluctuations in the temporal signal $\alpha_i(t), i \in [1; n_{exp}]$, each *stochastically independent* experiment i is fully characterized by $\hat{\phi}_i$, determined by Equation 6. The likelihood function is then given by Equation 14:

$$f\left(\{\hat{\phi}_i ; i \in [1; n_{exp}]\} \mid E_a\right) = \prod_{i=1}^{n_{exp}} f(\hat{\phi}_i \mid E_a). \tag{14}$$

Let us now consider a prior probability density $f_{E_a,0}(E_a)$, which represents our initial knowledge of E_a i.e. our degrees of belief about the likely and unlikely values of E_a before having seen any measurements. The posterior probability density is obtained by combining the prior and the likelihood using Bayes' theorem (Equation 15):

$$f_{E_a|\{\hat{\phi}_i\}}(E_a \mid \{\hat{\phi}_i\}) = \frac{f\left(\{\hat{\phi}_i\} \mid E_a\right) \cdot f_{E_a,0}(E_a)}{\int_{E_a=E_{a,min}}^{E_{a,max}} f\left(\{\hat{\phi}_i\} \mid E_a\right) \cdot f_{E_a,0}(E_a)\, dE_a}. \tag{15}$$

Here:

- $f_{E_a|\{\hat{\phi}_i\}}(E_a \mid \{\hat{\phi}_i\})$ is the posterior density of E_a given the observed data $\{\hat{\phi}_i\}$,

- $f\left(\{\hat{\phi}_i\} \mid E_a\right)$ is the likelihood function, as defined in Equation 14,

- $f_{E_a,0}(E_a)$ is the prior probability density of E_a.

- The denominator ensures normalization so that the posterior density integrates to 1.

The posterior density $f_{E_a|\{\hat{\phi}_i\}}(E_a \mid \{\hat{\phi}_i\})$ provides an updated estimation of the activation energy E_a, based on prior knowledge and experimental data: our degrees of belief about the likely values of E_a evolve upon seeing experimental evidence that usually favours some intervals of E_a values over others.

If we know only that an unknown parameter belongs to an interval, here $E_a \in [E_{a,\min} = 1 \times 10^4; E_{a,\max} = 2 \times 10^4]$ J/mol, precise Bayesian methods typically use a uniform prior over E_a by applying the principle of indifference [9], such that all values of E_a are considered to be equally likely:

$$f_{E_a,0}(E_a) = \frac{1}{E_{a,\max} - E_{a,\min}}. \qquad (16)$$

Based on the prior or the posterior $f_{E_a}(E_a)$, we can then compute the expected value

$$E(E_a) = \int_{E_a=E_{a,\min}}^{E_{a,\max}} E_a \cdot f_{E_a}(E_a)\, dE_a, \qquad (17)$$

and given a level of precision λ (such as $\lambda = 0.01$ we shall use in the remainder of this document), we can compute the credible interval $[C_{E_a,\text{infinite}}, C_{E_a,\sup}]$ holding $E(E_a)$ so that

$$p(E_a \in [C_{E_a,\mathbf{inf}}, C_{E_a,\sup}]) = 1 - \lambda. \qquad (18)$$

This implies that the lower and upper bounds of the credible interval can be calculated by solving the following equations for $C_{E_a,\mathbf{inf}}$ and $C_{E_a,\sup}$:

$$\int_{E_a=E_{a,\min}}^{C_{E_a,\mathbf{inf}}} f_{E_a}(E_a)\, dE_a = \frac{\lambda}{2}, \qquad (19)$$

$$\int_{E_a=C_{E_a,\sup}}^{E_{a,\max}} f_{E_a}(E_a)\, dE_a = \frac{\lambda}{2}. \qquad (20)$$

These integrals define the cumulative distribution function of $f_{E_a}(E_a)$ at the bounds of the credible interval.

As we saw in 2.1, we are primarily interested in predicting the delay time t_d such that $\alpha(t_d) = 0.80$ under the *non-isothermal* conditions outlined in 2.1 by relying upon isothermal trials to estimate E_a. Given that all other parameters are fixed and known, we can write that for a given E_a,

$$t_d = g(E_a) \qquad (21)$$

where g is a *monotonous* function that has no analytical expression (under non-isothermal conditions) but can only be known by numerically solving the differential equation

$$\frac{d\alpha}{dt} = \phi_{E_a}(T(t))\frac{3V_{mA}}{r_{0,desired}}(1-\alpha)^{2/3}. \qquad (22)$$

We approximated the function g with a satisfying level of accuracy by cubic spline interpolation validated by an independent test dataset. Knowing the PDF of E_a, $f_{E_a}(E_a)$, we can then compute the PDF of t_d using the following transformation. The relationship between t_d and E_a is given by $t_d = g(E_a)$, so the PDF of t_d, $f_{t_d}(t_d)$, can be derived as:

$$f_{t_d}(t_d) = f_{E_a}(E_a)\left|\frac{dE_a}{dt_d}\right|. \qquad (23)$$

Since $t_d = g(E_a)$, we need to numerically compute the inverse function $E_a = g^{-1}(t_d)$ and the derivative $\frac{dE_a}{dt_d}$. Thus, the PDF of t_d is:

$$f_{t_d}(t_d) = f_{E_a}(g^{-1}(t_d))\left|\frac{d}{dt_d}g^{-1}(t_d)\right|. \qquad (24)$$

The expression for $f_{t_d}(t_d)$ was validated through Monte Carlo simulations, which involved generating a large number of values of $E_a \sim f_{E_a}(E_a)$, calculating the corresponding delay times $t_d = g(E_a)$, and then computing the empirical PDF of t_d. The resulting empirical PDF was subsequently compared to the semi-analytical one.

This allows us to compute the probability density of t_d given the prior or posterior distribution of E_a. Following the same approach as above, we can then compute the expected value $E(t_d)$ and a confidence interval $[C_{t_d,\mathbf{inf}}, C_{t_d,\sup}]$ holding $E(t_d)$ so that

$$p(t_d \in [C_{t_d,\mathbf{inf}}, C_{t_d,\sup}]) = 1 - \lambda.$$

Due to drastic changes of the likelihood function across several orders of magnitude, numerical underflow becomes a critical issue when evaluating the posterior density. In particular, for certain values of E_a, the likelihood $f(\{\hat{\phi}_i\} \mid E_a)$ can drop below machine precision. To address this, the posterior is computed in logarithmic form. Starting from Bayes' theorem:

$$f_{E_a|\{\hat{\phi}_i\}}(E_a) = \frac{f(\{\hat{\phi}_i\} \mid E_a) \cdot f_{E_a,0}(E_a)}{\int_{E_{a,\min}}^{E_{a,\max}} f(\{\hat{\phi}_i\} \mid \xi) \cdot f_{E_a,0}(\xi)\, d\xi}, \qquad (25)$$

we first compute the log-posterior up to a constant:

$$\log f_{E_a|\{\hat{\phi}_i\}}(E_a) = \log f(\{\hat{\phi}_i\} \mid E_a) + \log f_{E_a,0}(E_a) + C, \qquad (26)$$

where C is an unknown normalisation constant. The unnormalised posterior is then obtained by exponentiating:

$$\tilde{f}_{E_a}(E_a) = \exp\left(\log f(\{\hat{\phi}_i\} \mid E_a) + \log f_{E_a,0}(E_a)\right), \qquad (27)$$

and finally normalised via:

$$f_{E_a|\{\hat{\phi}_i\}}(E_a) = \frac{\tilde{f}_{E_a}(E_a)}{\int_{E_{a,\min}}^{E_{a,\max}} \tilde{f}_{E_a}(\xi)\,d\xi}. \qquad (28)$$

In practice, when the likelihood falls below machine precision, it is truncated and set to 10^{-300}. This approximation introduces minor numerical inaccuracies, but these do not significantly affect the qualitative conclusions of our analysis. Nonetheless, future work should aim to enhance numerical accuracy.

In the next subsection 2.3, we will discuss why the precise Bayesian approach presented here can be deeply problematic.

2.3. Imprecise Bayesianism. If we know only that

$$E_a \in [E_{a,\min} = 1 \times 10^4, E_{a,\max} = 2 \times 10^4]\,\text{J/mol},$$

then we are equally ignorant about the transformed parameter

$$y = \frac{1}{E_a},$$

such that

$$y \in \left[\frac{1}{2 \times 10^4}, \frac{1}{10^4}\right]\,\text{mol/J}.$$

By applying the principle of indifference to y, we obtain a uniform prior:

$$f_{y,0}(y) = \begin{cases} \dfrac{1}{\frac{1}{10^4} - \frac{1}{2 \times 10^4}}, & y \in \left[\frac{1}{2 \times 10^4}, \frac{1}{10^4}\right], \\ 0, & \text{otherwise.} \end{cases} \qquad (29)$$

The prior densities $f_{E_a,0}(E_a)$ and $f_{y,0}(y)$ must be consistent under the transformation $y = \frac{1}{E_a}$. Using the change-of-variables formula, the prior for y can also be expressed as:

$$f_{y,0}(y) = f_{E_a,0}(E_a) \cdot \left|\frac{dE_a}{dy}\right| = f_{E_a,0}\left(\frac{1}{y}\right) \cdot \frac{1}{y^2}. \qquad (30)$$

Substituting $f_{E_a,0}(E_a)$ from the uniform prior assumption:

$$f_{y,0}(y) = \begin{cases} \dfrac{1}{E_{a,\max} - E_{a,\min}} \cdot \dfrac{1}{y^2}, & y \in \left[\frac{1}{2 \times 10^4}, \frac{1}{10^4}\right], \\ 0, & \text{otherwise.} \end{cases} \qquad (31)$$

However, this results in a contradiction because $f_{y,0}(y)$ is not uniform, as required by the principle of indifference applied to y. Instead, it is proportional to $\frac{1}{y^2}$, violating the assumption of equal ignorance about y.

To illustrate this inconsistency, let us calculate the probability that $E_a \in [1.05 \times 10^4, 1.10 \times 10^4]$ under these two priors.

For the uniform prior on E_a:.

$$P(E_a \in [1.05 \times 10^4, 1.10 \times 10^4]) \qquad (32)$$

$$= \int_{1.05 \times 10^4}^{1.10 \times 10^4} f_{E_a,0}(E_a)\,dE_a \qquad (33)$$

$$= \frac{(1.10 - 1.05) \times 10^4}{E_{a,\max} - E_{a,\min}} \qquad (34)$$

$$= \frac{0.05 \times 10^4}{(2 - 1) \times 10^4} = 0.05. \qquad (35)$$

For the uniform prior on y:. The corresponding interval for y is:

$$y \in \left[\frac{1}{1.10 \times 10^4}, \frac{1}{1.05 \times 10^4}\right].$$

The probability becomes:

$$P(E_a \in [1.05 \times 10^4, 1.10 \times 10^4]) \qquad (36)$$

$$= \int_{\frac{1}{1.10 \times 10^4}}^{\frac{1}{1.05 \times 10^4}} f_{y,0}(y)\,dy \qquad (37)$$

$$= \int_{\frac{1}{1.10 \times 10^4}}^{\frac{1}{1.05 \times 10^4}} \frac{1}{\frac{1}{10^4} - \frac{1}{2 \times 10^4}}\,dy \qquad (38)$$

$$= \frac{\frac{1}{1.05 \times 10^4} - \frac{1}{1.10 \times 10^4}}{\frac{1}{10^4} - \frac{1}{2 \times 10^4}} \qquad (39)$$

$$= \frac{(1.10 - 1.05)/(1.05 \cdot 1.10) \times 10^4}{0.5} \approx 0.0866. \qquad (40)$$

The two probabilities differ significantly:

$$P_{\text{uniform in } E_a} \approx 0.0500,$$
$$P_{\text{uniform in } y} \approx 0.0866,$$

demonstrating that the priors $f_{E_a,0}(E_a)$ and $f_{y,0}(y)$ cannot both be uniform and that the degrees of belief about E_a, which we are expected to hold as precise Bayesians, are inconsistent.

Additionally, we could consider other parameter transformations, such as $\log_{10}(E_a)$, $\frac{1}{\log_{10}(E_a)}$, E_a^2, and $\frac{1}{E_a^2}$. These transformations are also inconsistent with one another, as a prior uniform with respect to one transformation is non-uniform with respect to others and epistemically, none of these variables can be favoured over another, so far as our ignorance is concerned. While Jeffreys' prior [12] would avoid the problem of the arbitrariness of the parametrisation, it would still be non-uniform with respect to at least several of the parametrisations we have just mentioned. Consequently, it would still introduce a lot of spurious specific knowledge unjustified by the only information we have at our disposal, namely the bounds of E_a. All of this highlights the problem with applying

the principle of indifference to transformed parameters and with other principles aiming at providing the user with a *single* so-called "ignorance-prior" [15]: they blur the distinction between knowledge and ignorance.

This leads us to two possible strategies for a *very simple* imprecise Bayesian analysis, accessible to skilled chemical experimentalists who may lack a strong background in probability theory and statistics:

- Consider *all* priors that are uniform with respect to E_a, $\log_{10}(E_a)$, $\frac{1}{\log_{10}(E_a)}$, E_a^2, or $\frac{1}{E_a^2}$.

- Use a discrete set of truncated normal priors $\{f_{0,\mu_{E_a},\sigma_{E_a}}(E_a)\}$ that equals 0 outside the interval $[E_{a,min}; E_{a,max}]$ and are normalised.

For each prior, we apply the methodology outlined in Section 2.2. The key quantities derived for each prior and its corresponding posterior (based on the likelihood and the $\hat{\phi}_i$) are $E(E_a)$ and $E(t_d)$.

By considering a discrete set of probability densities of E_a (whether priors or posteriors), $\{f_{E_a,i}(E_a), i \in [1,m]\}$, we compute:

$$\min_{i\in[1,m]}\Big(E_i(E_a)\Big) \text{ and } \max_{i\in[1,m]}\Big(E_i(E_a)\Big),$$

and similarly:

$$\min_{i\in[1,m]}\Big(E_i(t_d)\Big) \text{ and } \max_{i\in[1,m]}\Big(E_i(t_d)\Big).$$

Both for the precise and imprecise Bayesian frameworks presented, we generated a large population $\{\hat{\phi}_j\}$, $j \in [1,200]$, using Equation (7):

$$r_0 = \frac{\phi \cdot \mu}{\hat{\phi}} \quad \text{so that} \quad \hat{\phi} = \frac{\phi \cdot \mu}{r_0},$$

by first generating the random numbers $r_0 \sim \text{logNormal}(\mu,\sigma)$ that are, given our scenario, the only cause of the non-repeatability of the isothermal experiments.

We will then consider a *series of experiment sets*, denoted as $Sets_{Exp}$.

For example, if $Sets_{Exp} = \{2,4,6\}$, the first set corresponds to the two first experiments $\{\hat{\phi}_1, \hat{\phi}_2\}$, the second set to the four first experiments $\{\hat{\phi}_1, \hat{\phi}_2, \hat{\phi}_3, \hat{\phi}_4\}$, and the third set to the six first experiments $\{\hat{\phi}_1, \hat{\phi}_2, \hat{\phi}_3, \hat{\phi}_4, \hat{\phi}_5, \hat{\phi}_6\}$.

For each prior, this would generate three posteriors, allowing us to evaluate the evolution of our (precise or imprecise) Bayesian analysis as the sample size grows.

3. RESULTS AND DISCUSSION

3.1. Precise Bayesianism. Using the same sample of 200 experiments mentioned in 2.3, we considered 8 *sets* of experiments characterised by the following sample sizes:
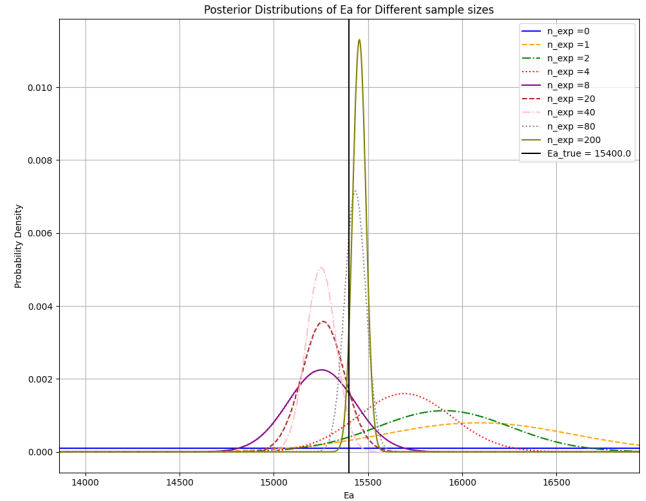

Figure 3. *Single uniform prior and posteriors for the different sample sizes with E_a in J/mol.*
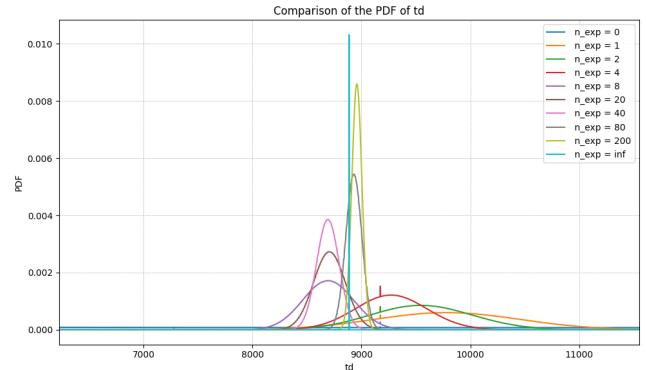

Figure 4. *PDF of t_d (s) for the different sample sizes.* ***infinite*** *stands for an infinite sample size that would lead to the true value.*

$Sets_{Exp} = \{1,2,4,8,20,40,80,200\}$. The prior and posteriors can be seen in Figure 3, whereas the probability density $f_{t_d}(t_d)$ corresponding to them can be visualised in Figure 4. The expected values of E_a and t_d, along with their credible intervals with a risk equal to $\lambda = 0.01$, are shown in Tables 1 and 2.

We can see that as the sample size n_{Exp} grows, the expected values $E(E_a)$ and $E(t_d)$ converge to the true values $E_{a,true}$ and $t_{d,true}$, which we would get for an infinite sample size, according to the law of large numbers [5].

3.2. Imprecise Bayesianism.

Uniform priors. We initially explored a set of priors that are uniform over different transformations of E_a, namely: E_a, $\log_{10}(E_a)$, $\frac{1}{\log_{10}(E_a)}$, E_a^2, and $\frac{1}{E_a^2}$. These priors are shown in Figure 5.

The outcomes of updating these uniform priors are summarised in Tables 3 and 4. For comparison purposes,

n_{Exp}	$E(E_a)$	$C_{E_a,inf}$	$C_{E_a,sup}$
0	15000.00	10050.00	19950.00
1	16083.69	14797.87	17368.45
2	15903.67	14993.97	16814.06
4	15693.62	15048.69	16335.89
8	15253.11	14798.95	15707.34
20	15262.00	14973.83	15548.83
40	15251.16	15047.15	15453.80
80	15432.69	15288.26	15575.69
200	15453.98	15362.35	15544.31
infinite	15400.00	15400.00	15400.00

Table 1. E_a (J/mol) estimate as a function of the sample size for one single uniform prior.

n_{Exp}	$E(t_d)$	$C_{t_d,inf}$	$C_{t_d,sup}$
0	8555.72	2849.45	10939.01
1	9792.55	8471.58	10298.76
2	9552.09	8472.01	9883.75
4	9273.72	8402.26	9512.61
8	8694.83	8110.24	9214.77
20	8706.12	8323.84	8827.21
40	8691.81	8421.16	8780.88
80	8929.97	8741.36	9796.86
200	8957.93	8839.60	9234.44
infinite	8887.01	8887.01	8887.01

Table 2. t_d (s) estimate as a function of the sample size for one single uniform prior.

the frequentist Maximum Likelihood Estimate (MLE_{E_a}) is also included.

n_{Exp}	$MLE(E_a)$	$\min(E(E_a))$	$\max(E(E_a))$
0	-	13333.33	15555.56
1	16084.88	16037.30	16099.54
2	15906.09	15882.22	15913.61
4	15693.78	15681.30	15697.22
8	15254.45	15247.13	15255.31
20	15264.45	15262.01	15265.27
40	15253.87	15251.24	15252.87
80	15435.09	15434.03	15434.84
200	15453.83	15453.74	15454.06
Infinite	15400.00	15400.00	15400.00

Table 3. MLE and lower and upper predictions for $E(E_a)$ (in J/mol) (set of uniform priors)

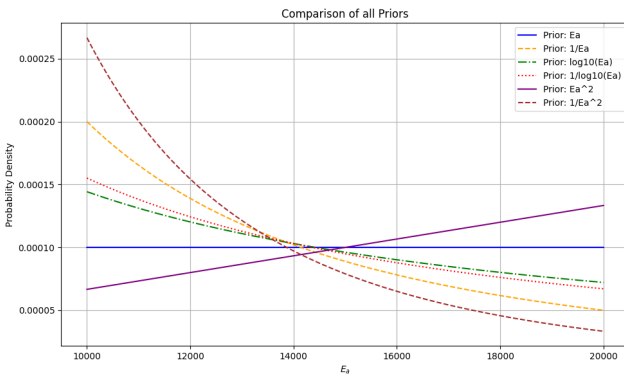**Figure 5.** Set of uniform priors with E_a in J/mol.

n_{Exp}	$\min(E(t_d))$	$\max(E(t_d))$
0	6508.15	9251.17
1	9731.11	9813.78
2	9523.87	9565.44
4	9257.55	9278.54
8	8686.95	8697.64
20	8706.11	8710.38
40	8691.90	8694.04
80	8931.73	8932.79
200	8957.62	8958.04
Infinite	8887.01	8887.01

Table 4. Lower and upper predictions for $E(t_d)$ (s) (set of uniform priors)
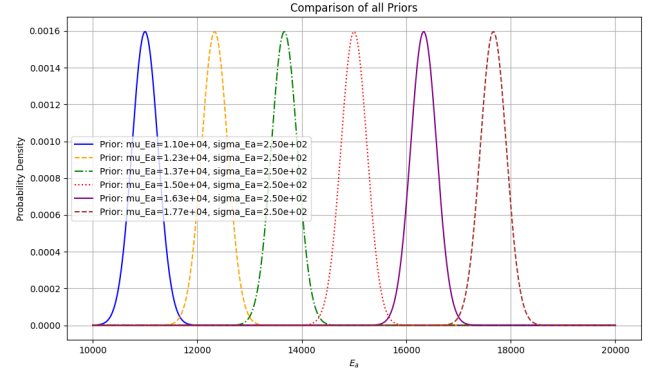

Figure 6. Set of truncated normal priors with E_a in J/mol.

Truncated normal priors. To model uncertainty with more flexibility, we consider a set of *n* truncated normal priors for E_a, constructed as follows:

- **Truncation bounds**: Each prior is restricted to $E_a \in [E_{a,min}, E_{a,max}]$.
- **Standard deviation**: The standard deviation σ_{E_a} of all priors is calculated using the formula:

$$\sigma_{E_a} = \frac{E_{a,max} - E_{a,min}}{40}. \tag{41}$$

- **Mean range**: The possible means μ_{E_a} are distributed uniformly within a reduced interval:

$$\mu_{E_a} \in \big[E_{a,\min} + 0.10 \cdot (E_{a,\max} - E_{a,\min}), \tag{42}$$
$$E_{a,\max} - 0.10 \cdot (E_{a,\max} - E_{a,\min}) \big]. \tag{43}$$

Using *n* equally spaced values of μ_{E_a} within this range, each corresponding to a truncated normal distribution, we ensure a balanced representation of uncertainty over E_a. Figure 6 visualises these priors for $n = 6$.

The key results of updating these truncated normal priors are detailed in Tables 5 and 6.

3.3. Discussion. We can see that for the precise Bayesian approach based on a single prior uniform with respect to E_a, for up to eight experiments, the estimate of the delay time t_d is still not very close to the true

n_{Exp}	$MLE(E_a)$	$\min(E(E_a))$	$\max(E(E_a))$
0	-	11000.03	17666.67
1	16084.88	13620.38	17349.48
2	15906.09	13471.22	17078.76
4	15693.78	13435.22	16679.01
8	15254.45	13839.19	16056.59
20	15264.45	14555.98	15663.23
40	15253.87	14868.35	15472.31
80	15435.09	15224.63	15540.56
200	15453.83	15366.82	15497.22
Infinite	15400.00	15400.00	15400.00

Table 5. *MLE and lower and upper predictions for $E(E_a)$ (in J/mol) (set of truncated normal priors)*

n_{Exp}	$\min(E(t_d))$	$\max(E(t_d))$
0	3741.80	11919.01
1	6625.90	11489.54
2	6445.63	11123.65
4	6402.74	10585.79
8	6893.82	9753.58
20	7792.74	9233.14
40	8193.74	8982.03
80	8657.00	9071.72
200	8843.44	9014.75
Infinite	8887.01	8887.01

Table 6. *Lower and upper predictions for $E(t_d)$ (s) (set of truncated normal priors)*

value (for $n_{exp} = 8$, $E(t_d|8 \text{ exps}) = 8694.83$ s instead of $t_{d,\text{true}} = 8887.01$ s), which can also cause a gap in the desired chemical yield. To be sure, for $n_{exp} = 8$, the credible interval $[C_{t_d,\text{inf}}; C_{t_d,\text{sup}}] = [8110.24; 9214.77]$ s is also relatively large. The problem is that precise Bayesian decision theory is entirely grounded in a *single* value that is often the *expected value* of the target variable [1]. If the agent uses a quadratic loss function to make a decision, they will choose to use $t_d = E(t_d|8 \text{ exps}) = 8694.83$ s to achieve the desired yield $\alpha_d = 0.80$. As a consequence, when it comes to rational actions, standard precise Bayesianism has a hard time making a distinction between what economist Keynes called the balance of the evidence and the weight of the argument [19], as the decision would have been the same if the credible interval had been much smaller or much larger.

Imprecise Bayesianism, on the other hand, can make such a distinction. For the set of truncated normal priors, for $n_{exp} = 8$, we have $[\min(E(t_d|8 \text{ exps})); \max(E(t_d|8 \text{ exps}))] = [6893.82; 9753.58]$ s. If they trust their set of priors, an imprecise Bayesian agent would only know that the delay time leading to the desired conversion belongs to that interval, and that might be a reason to conduct additional experiments to narrow it down further. At this point, it is worth noting that if the agent had relied on the set of uniform priors instead, they would have ended up believing that $[\min(E(t_d|8 \text{ exps})); \max(E(t_d|8 \text{ exps}))] = [8686.95; 8697.64]$ s, which is a much smaller but *potentially* misleading interval. The explanation for this can be
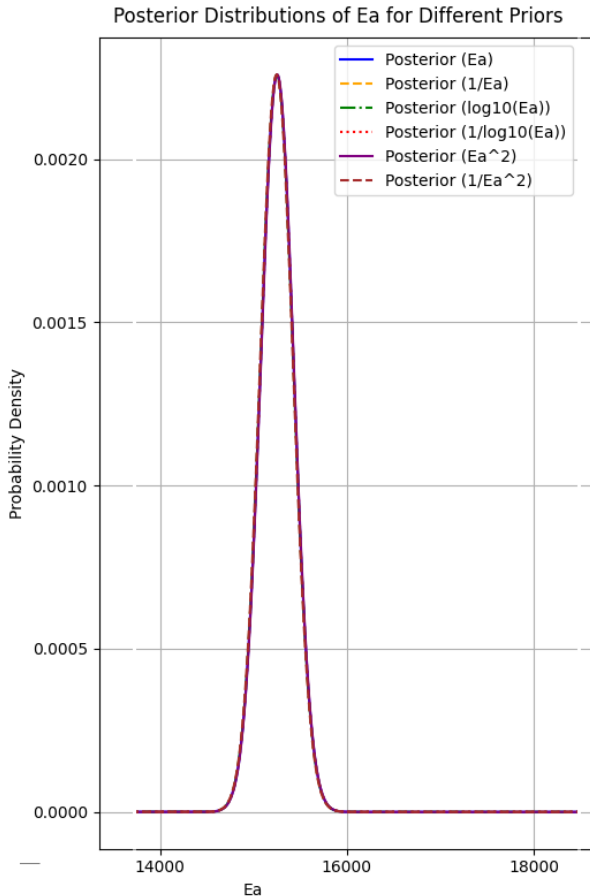

Figure 7. *Posteriors for $n_{exp} = 8$ and the set of uniform priors, E_a in J/mol*

found in Figure 7 which shows the posteriors obtained for $n_{exp} = 8$ and the uniform priors and 8 which shows the corresponding posteriors for the truncated normally distributed priors. Unlike the discrete set of truncated normal priors, the discrete set of uniform priors quickly behaves like a single prior after n_{Exp} has exceeded a given threshold. This behaviour stems from the fact that the likelihood function changes rapidly across several orders of magnitude, such that the influence of a prior with only polynomial variation becomes negligible in the posterior. On the other hand, truncated normal priors require much more data to converge towards the same probability distribution, as they too change rapidly across several orders of magnitude. However, care must be taken not to choose too extreme truncated normal priors in the set, as we may then approach a situation of belief inertia [26] where even strong evidence stemming from a large number of experimental trials would only have very small effects on the lower and upper previsions for posterior expected values of the quantities that matter to us.
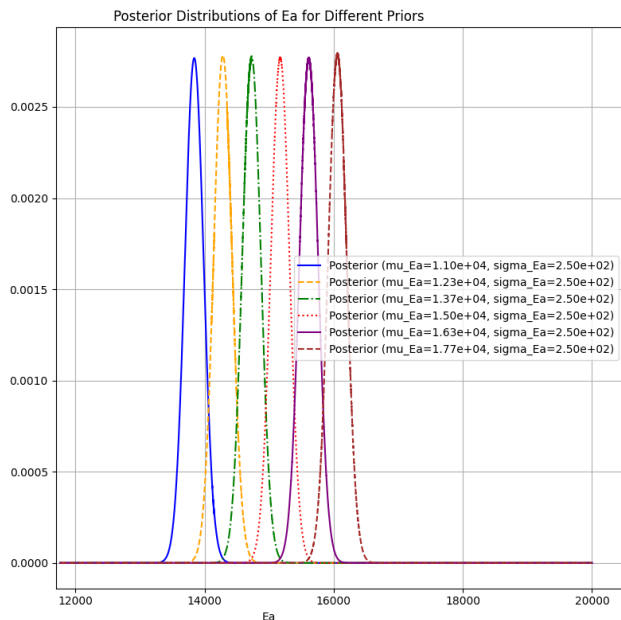
Figure 8. *Posteriors for $n_{exp} = 8$ and the set of truncated normal priors, E_a in J/mol*

4. Conclusion

To the best of our knowledge, this is the first time that an imprecise Bayesian framework has been applied to the problem of gas-solid reaction kinetics. We were able to successfully transfer the experimental uncertainty originating from the random variation of the radius of the particles in the powder samples used for isothermal experiments to the uncertainty of the activation energy E_a, and then to the uncertainty in the delay time t_d at which a conversion degree of 80% is reached under non-isothermal conditions and for a different but fixed particle size. We were further able to show that, while it is problematic to rely on a single uniform prior as objective precise Bayesians usually do, considering a set of uniform priors (as was done in [7, 10]) is also problematic if the magnitude of their variation is very small in comparison to the magnitude of the variation of the likelihood function. Considering a discrete set of (truncated) normal distributions with different mean values and the same standard deviation appeared to be a better choice, as they too vary across several orders of magnitude and their differences are significant enough to lead to different posterior previsions for the optimal t_d when the number of experiments is not large enough to be trusted to make important decisions.

Nevertheless, this preliminary work relied on several simplistic assumptions that allowed us to consider a very idealised situation that is unlikely ever to be encountered in practice. To make such a study more realistic, the following steps can be followed:

- It very seldom happens that one kinetic parameter is exactly known, whereas the other one is considerably uncertain. In a future study, both A and E_a should be considered unknown and estimated via isothermal experiments conducted at different temperatures.

- Rather than being characterised by a single radius r_0, a 10 mg sample of powder should be characterised by a normal or lognormal probability density, whose parameters are themselves random variables that vary from sample to sample.

- We assumed that the "experimental" data represent the exact solution of a differential equation. In practice, it often displays random fluctuations as a function of time that also ought to be taken into account.

- A more ambitious goal of such uncertainty propagation studies should be to estimate the uncertainties related to the optimisation of gas-solid pilot-scale reactors relevant to the industrial world, such as a rotary kiln [17] or a fluidised bed [22], via Computational Fluid Dynamics (CFD) simulations [3]. These simulations combine the equations of fluid mechanics, heat transfer, and chemical kinetics and handle their complex interactions.

- For the imprecise Bayesian analysis, it would make much more sense to consider a continuous set of truncated normal or lognormal priors, such as the method developed by Quaeghebeur and De Cooman [21], rather than a discrete one. Unfortunately, since the likelihood is not an analytical function, it is not possible to find a series of conjugate priors and to derive neat analytical formulae allowing one to update the parameters of such priors with a sufficient statistic reducing the experimental data to a single real number. As a result, the mathematical problem of determining lower and upper previsions for a continuous family of non-analytical probability distributions could prove quite complex and challenging.

- Until now, there are virtually no studies comparing the particle size distributions (PSDs) of multiple small samples of powders used in gas-solid chemical kinetic experiments conducted in a thermobalance or similar devices. Preliminary results obtained in our lab suggest that the PSDs vary stochastically from one powder sample to another. However, a rigorous quantification of this phenomenon would be necessary to apply our uncertainty propagation method to a real-world case.

- Given the considerably higher mathematical complexity of realistic chemical systems, more performing and efficient techniques for updating a set of priors and computing the posterior expected values

of different variables must be utilised. The combination of iterative importance sampling with Markov-Chain-Monte-Carlo sampling [4] is one of these promising approaches we intend to consider for our next research projects.

- When dealing with a likelihood function that swiftly changes by many orders of magnitude, more sophisticated and accurate methods than a simple cut-off value and logarithmic transformation need to be developed. Furthermore, the numerical technique used to derive the PDF of the delay time t_d out of the PDF of the activation energy E_a is not always very accurate numerically and there is also a need to resort to a more advanced approach. The approximations we have used for this purely numerical study appears to be unproblematic for qualitatively comparing probabilistic methods based on a synthetic dataset and a simplified case. Nevertheless, it could become a serious issue when dealing with real-world data, a much more complex system, and a reactor to be designed and optimised.

Additional author information

Competing interests. No competing interests have to be declared for this purely theoretical study.

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