

On the usefulness of imprecise Bayesianism in chemical kinetics

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Introduction

- Chemical kinetics: study of the speed of chemical reactions and the factors bearing on it [1].
- Application to a wide range of fields: combustion, catalysis, atmospheric chemistry, water pollution...
- The ultimate goal is to derive predictive models.
- Both frequentist and Bayesian approaches are used to describe and propagate the parameter uncertainty [2,3].
- Unfortunately, they're applied mostly uncritically without being aware of fundamental issues.
- Most preoccupying of all is the researchers' massive reliance on a single (mostly uniform) prior to describe ignorance [4,5].

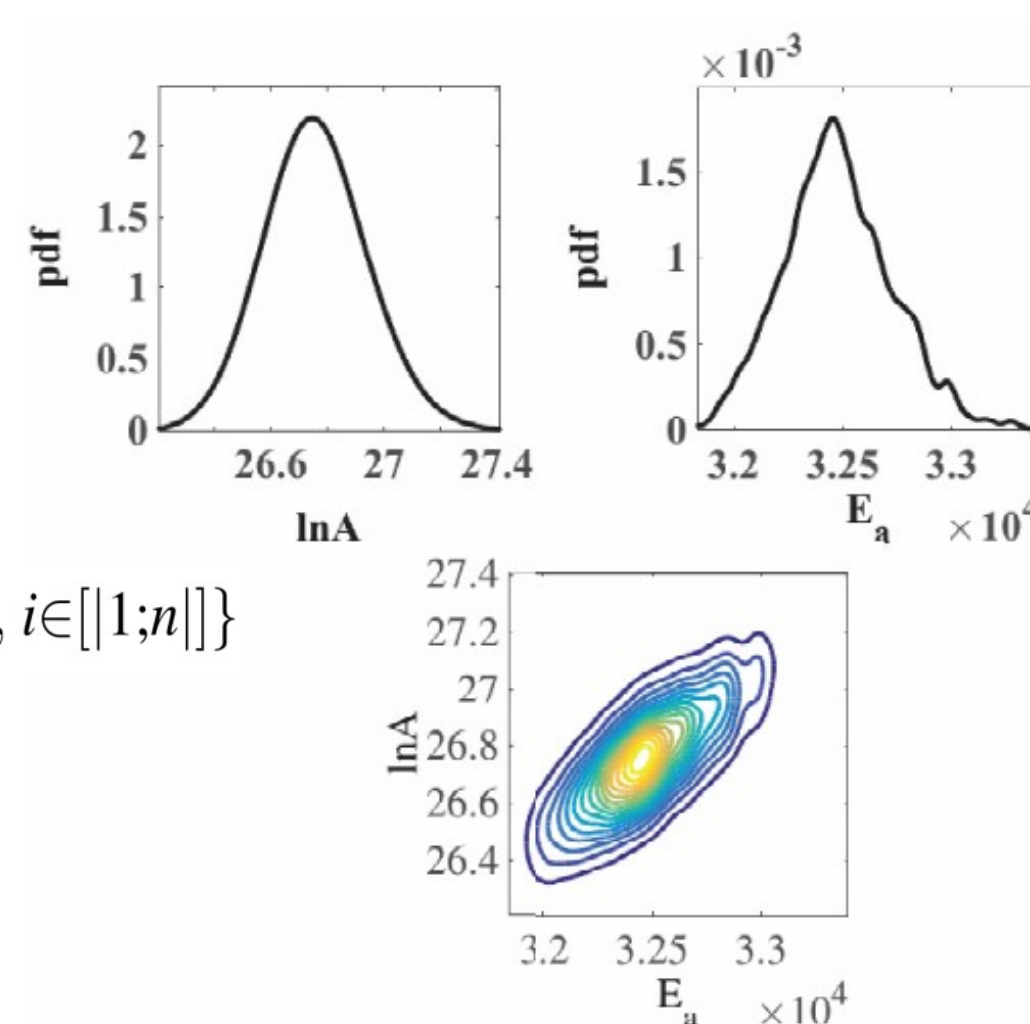
Basics

• Reaction $\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$ $r = \frac{1}{\nu_A} \frac{d[A]}{dt} = \frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_C} \frac{d[C]}{dt} = \frac{1}{\nu_D} \frac{d[D]}{dt} = k[A]^{\nu_A}[B]^{\nu_B} = AT^n \exp\left(\frac{-E_A}{RT}\right)[A]^{\nu_A}[B]^{\nu_B}$

A: Pre-exponential factor. E_A : Activation energy. n : Temperature coefficient.

R: Ideal gas constant. ν_j is always positive for products and negative for reactants.

• If there are N_s elementary reactions, ODE: $\frac{d[A]}{dt} = \sum_{j=1}^{j=N_s} \nu_{j,A} r_j$



• Frequentism: Feasible Set Approach. $F = \{k \mid p(|X_i(m_i(k)) - m_i(k)| \geq |e_i - m_i(k)|) \geq \alpha, i \in [1;n]\}$

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

n : number of measurements.

• Bayesianism: $f(k|e) = \frac{L(e|k)f_0(k)}{\int_{k \in K} L(e|k')f_0(k')dk'}$ $L(e|k)$: likelihood $f_0(k)$: prior

The problem of the priors

- The major problem of precise Bayesianism is the choice of the prior.
- In chemical kinetics, almost all practitioners use one single uniform prior.
- But this involves mistaking ignorance for knowledge.
- $p(\text{head}) = 0.5$ means we do know that a coin is perfectly symmetric. It cannot also mean we know absolutely nothing about the coin.
- The uniformity of a prior always depends on the parametrisation.
- A prior uniform with respect to k can be highly non-uniform with respect to $\log_{10}(k)$ or k^c .
- Main difference between frequentism and precise Bayesianism: Ockham's razor.
- **Ockham's razor**: "All other things being equal, simpler models are more likely to be true than more complex ones".



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

Uniform prior \rightarrow

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

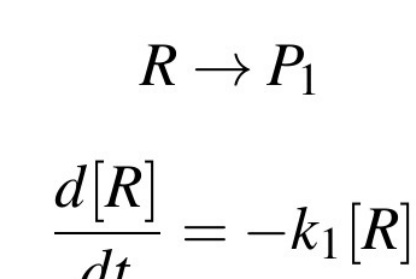
$$F = \frac{L_{\max}(E|k_2)}{L_{\max}(E|k_1)} \quad \text{: maximum likelihood ratio.} \quad O = \frac{V_{PM2}}{V_{PM1}} \quad \text{: Ockham's factor.}$$

- The larger V_{M1} is in comparison to V_{M2} , the likelier M_2 becomes.
- This, however, assumes that a uniform prior is a legitimate expression of ignorance.
- O is strongly dependent on the parametrisation [6].

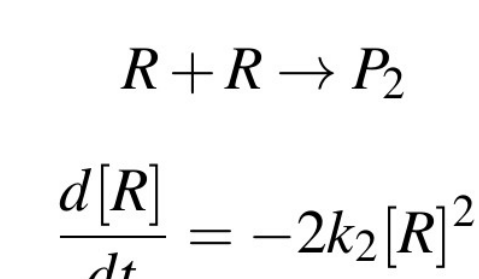
Application to a simple case

Two reaction models, one experimental profile

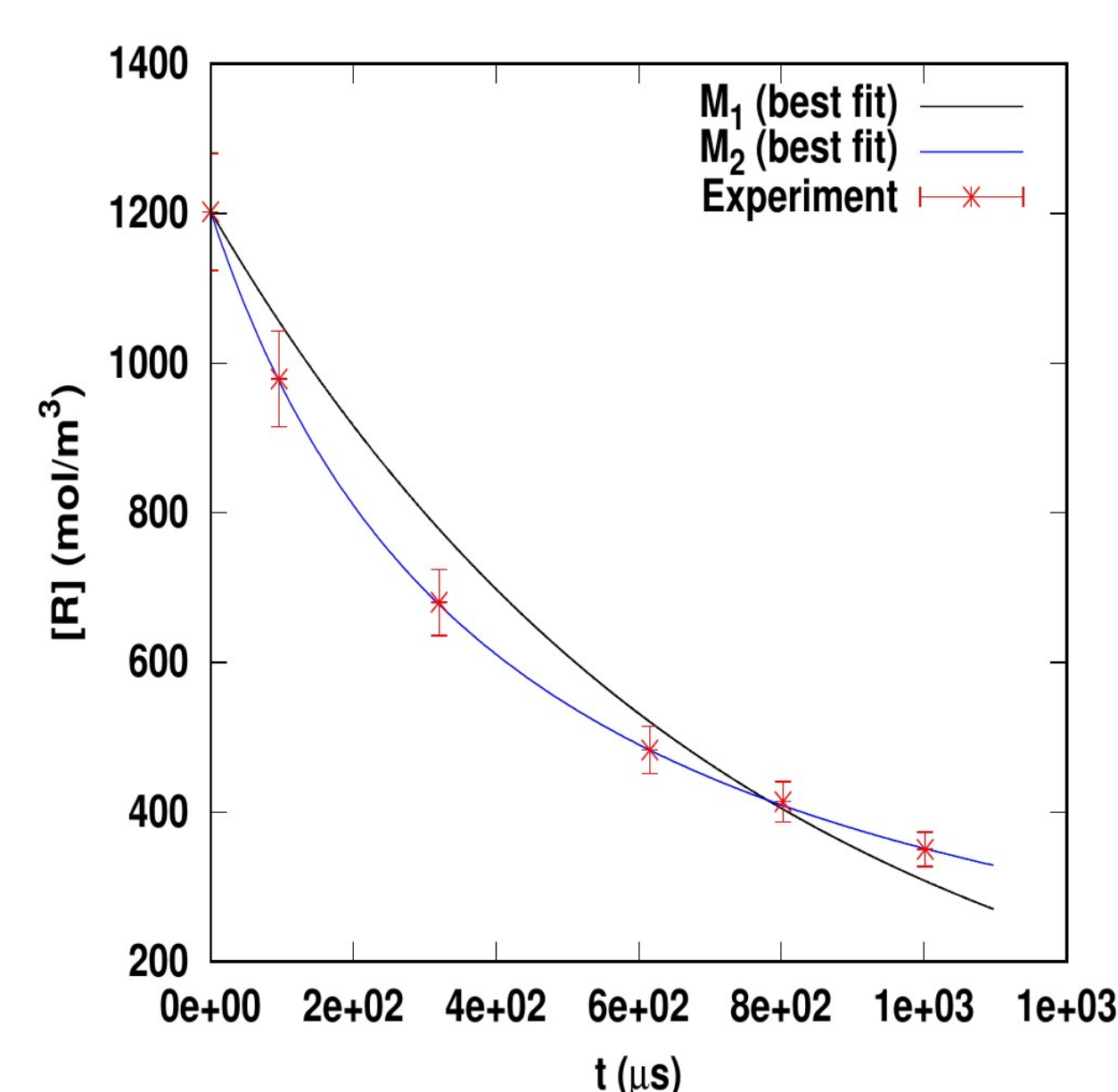
• M_1 : An isomerisation towards product P_1



• M_2 : A recombination towards product P_2



Frequentism



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

$$M_1: F_e = \{\emptyset\}$$

$$M_2: F_e = [8.51E+05; 1.22E+06] \text{ mol. cm}^{-3} \cdot \text{s}^{-1}$$

Precise Bayesianism

• Uniform prior $\rightarrow P(k_1|M_1) = 0.00050$
 $P(k_2|M_2) = 1/(5^9 - 5^4) = 2^{-10} \rightarrow B = 0.312$

- We should reject model M_2 in favour of model M_1 in spite of the poor agreement!
- Lindley's paradox: mixture of knowledge (likelihood) with ignorance (prior) [7].

Imprecise Bayesianism

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

Dependency of O and B on the prior

\rightarrow **conclusion strongly dependent on the prior!**

Conclusion

- Bayesianism brings lots of exciting possibilities into chemical kinetics.
- However, the reliance on one single prior undermines the reliability of the results.
- Yet, the large majority of chemical kineticists use precisely such a single uniform prior!
- There is an urgent need for robust Bayesian analyses embedded in an imprecise framework.

References

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