Inference of H_2O_2 thermal decomposition rate parameters from experimental statistics

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Motivation

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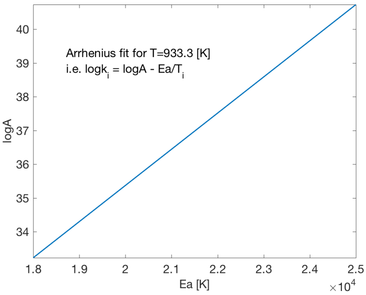
- UQ perspective: ideally infer the uncertainty in model parameters given said model and data to arrive at a (posterior) parameter PDF
- Is it still possible to conduct this inference in the absence of data?

Rate parameters - correlation

- How uncertainty is reported is crucial. Arrhenius parameter uncertainty is often highly correlated and this is typically not reported



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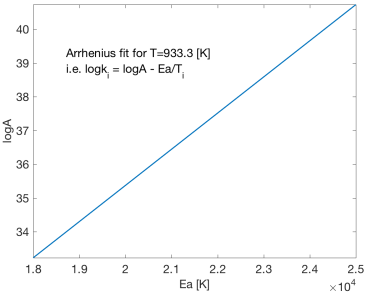

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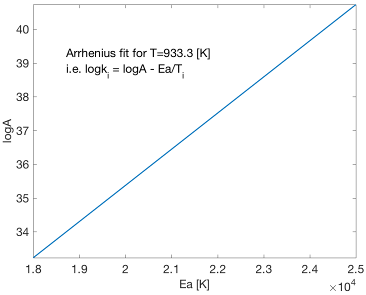

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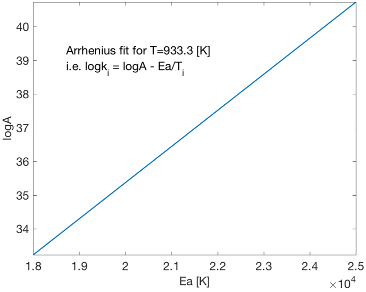

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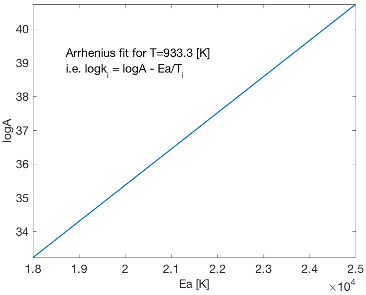
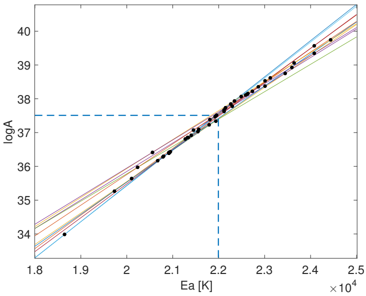
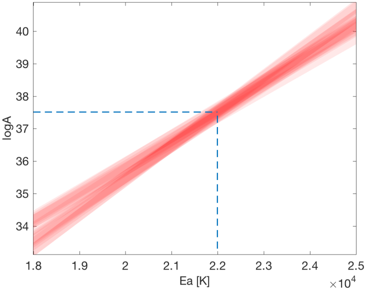




In reality no consensus due to model inadequacy and/or data error, require regression to find 'best-fit' Arrhenius parameters

Rate parameters - correlation

- Same picture when including uncertainty



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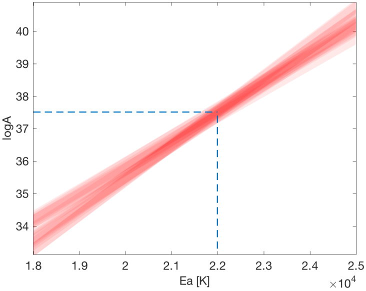

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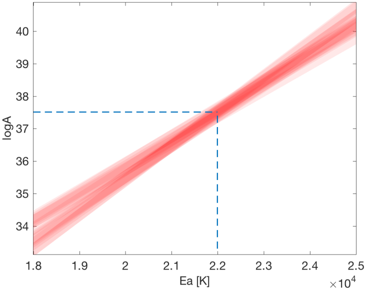

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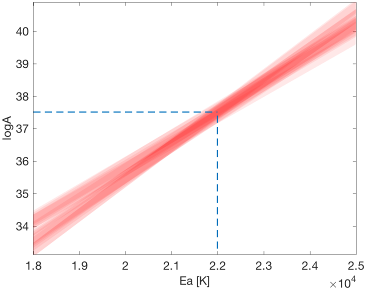

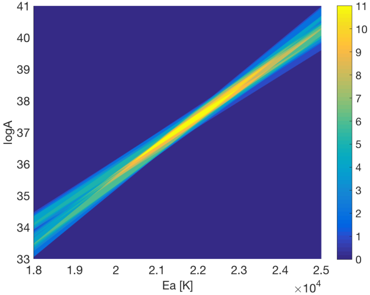

Summing the overlaps gives some notion of an approximate parameter density. In the limit of infinite experimental temperature stations could arrive at a PDF. Regardless, parameter correlation is strongly expressed.

Data and parameter inference

- Data and parameter inference procedure proposed by Berry et al. [1] based on maximum entropy arguments and utilizing Approximate Bayesian Computation (ABC) methods [2]

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- Pose problem in a Bayesian framework to explore data space to discover consistent data sets
- Algorithm composed of an outer inference on data subject to constraints, with a nested inner inference on parameters (rate coefficients and data error variance) with an error model

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Bayesian framework

Bayes' Law

$$p(A,B) = p(A|B)\,p(B) = p(B|A)\,p(A)$$

$$\Rightarrow p(A|B) = \frac{p(B|A)p(A)}{p(B)}$$

Bayesian framework

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$$p\left(A,B\right)=p\left(A|B\right)p\left(B\right)=p\left(B|A\right)p\left(A\right)$$

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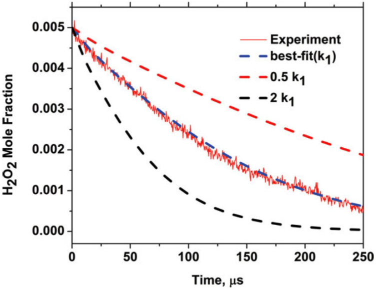
Bayesian Inference

$$p\left(A|B\right)\propto p\left(B|A\right)\pi\left(A\right)$$

$p\left(A|B\right)$: posterior distribution of A given information B
$p\left(B|A\right)$: likelihood function, probability that A is consistent with B
$\pi\left(A\right)$: prior distribution of A

H_2O_2 decomposition - target experiment

- $H_2O_2 + M \longrightarrow 2\,OH + M$
  consider low pressure results



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1.15	1012.5	0.42
1.08	1186.8	0.45
2.33	997.54	0.47
2.35	1166.6	0.50

Table: Experimental conditions

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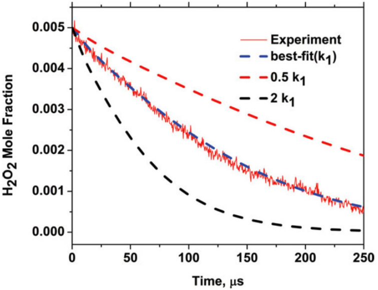

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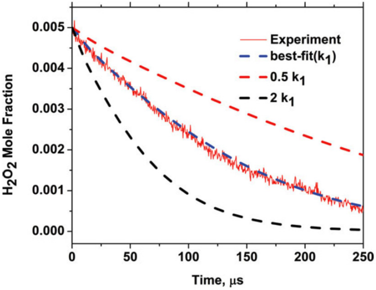

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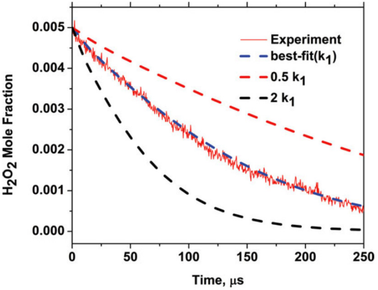

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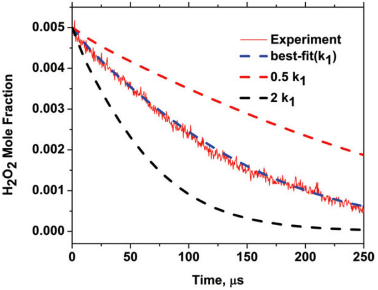
- Data are concentration vs. time decay profiles of H_2O_2 derived from the device signal
- Reported fit:
  $k(T)=10^{16.29\pm0.12}\exp(-21993\pm301/T)$



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Data and parameter inference procedure

Missing data model (Gaussian error/noise, $\varepsilon \sim \mathcal{N}(0,1)$):

$$[\mathrm{H_2O_{2data}}] = [\mathrm{H_2O_{2model}}] + \sigma\varepsilon$$

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Parameter inference (to establish $S_{\mathbf{D}}$), parameter likelihood:

$$p(\lambda|\mathbf{D}) = \frac{p(\mathbf{D}|\lambda)\pi(\lambda)}{p(\mathbf{D})} \qquad p(\mathbf{D}|\lambda) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{\left([\mathrm{H_2O_{2data}}]_{i,j} - [\mathrm{H_2O_{2model}}]_{i,j}\right)^2}{2\sigma^2}\right)$$

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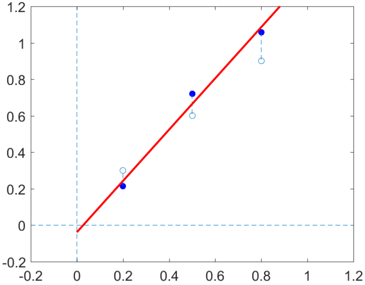
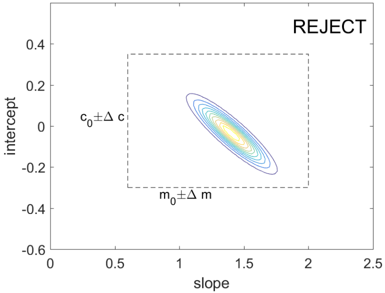
Knowledge of the posterior PDFs are constructed using Markov Chain Monte Carlo sampling for both the outer (data) and inner (parameter) inference.

Data inference - parameter line model

Data model:

$$y_{data} = y_{model} + y_{error} = mx + c + y_{error} \tag{1}$$

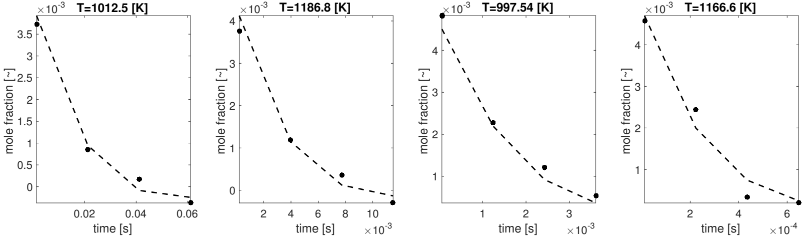




Accept data consistent with constraints, i.e. mean line slope and intercept (m_0, c_0) and marginal error bars on m,c, interpreted as standard deviations

Inferred H_2O_2 data

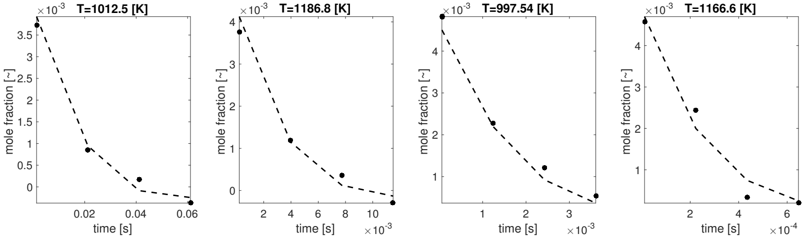
- Replicate the context of the experiment as closely as possible based on reported information



Consistent data sample arrising from the data inference procedure (dashed lines are model predictions using nominal rate parameters).

Inferred H_2O_2 data

- Replicate the context of the experiment as closely as possible based on reported information
- Use identical chemical mechanism and thermochemistry database for forward model



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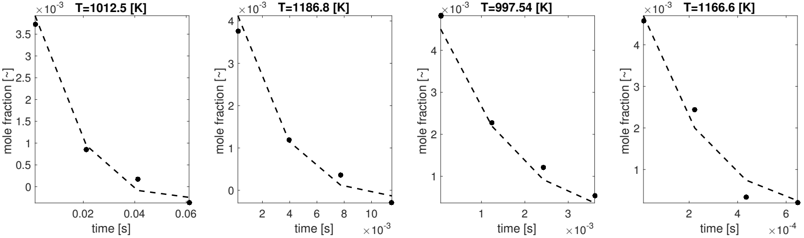

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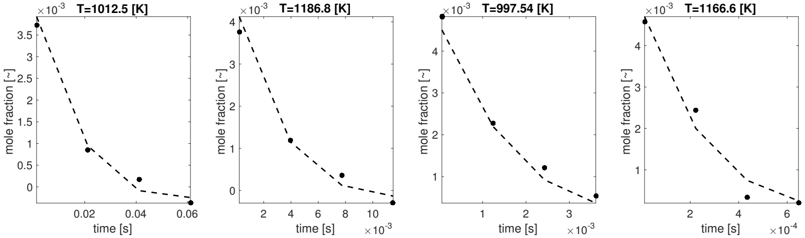

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Pooled parameter PDF

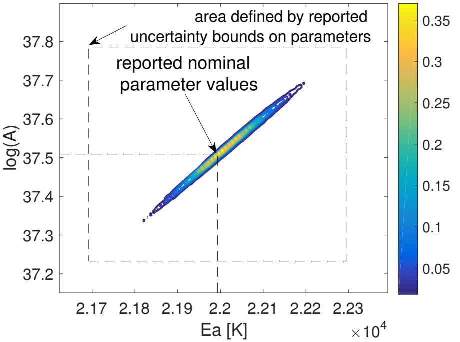

Figure: contours of probability density, joint parameter posterior PDF

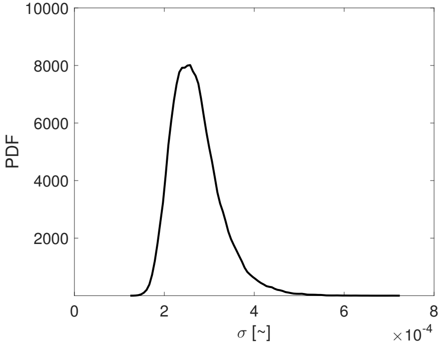

Figure: marginal PDF of data error

- marginalize over data in joint data-parameter posterior

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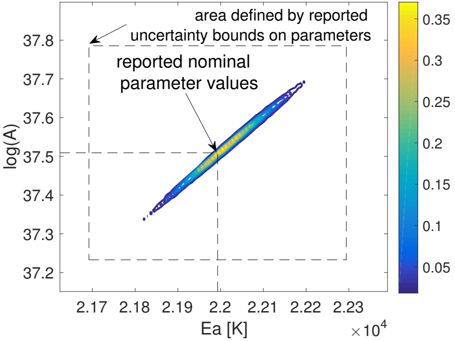

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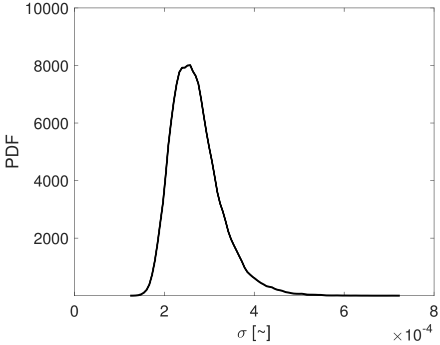

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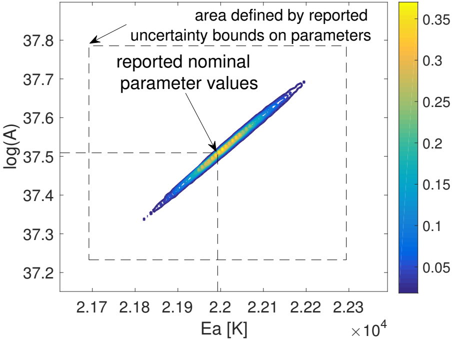

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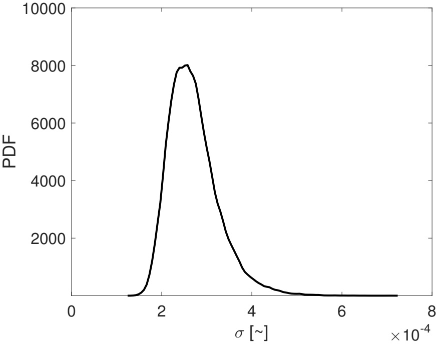

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- nominal values occur in regions of high probability mass

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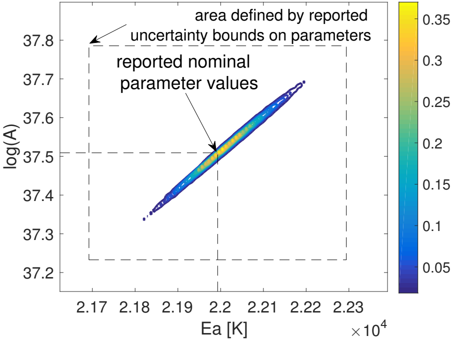

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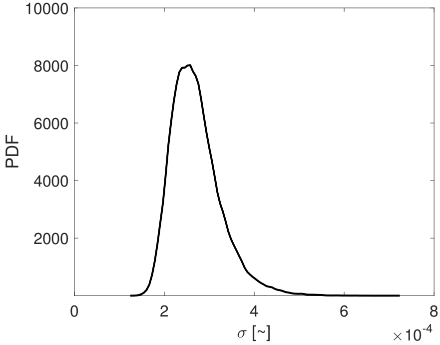

Figure: marginal PDF of data error

- marginalize over data in joint data-parameter posterior
- PDF reveals parameter correlation
- nominal values occur in regions of high probability mass
- noise amplitude is also inferred

Application: H_2-O_2 explosion limits

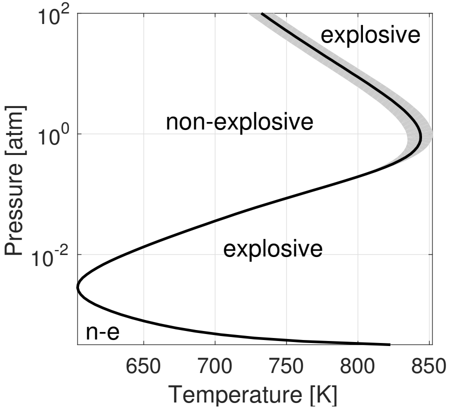

Figure: stoichiometric H_2-O_2 explosion limit curve

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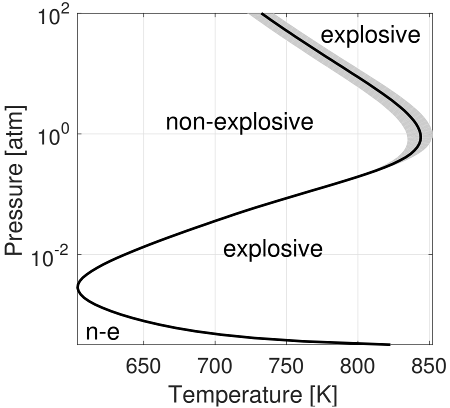

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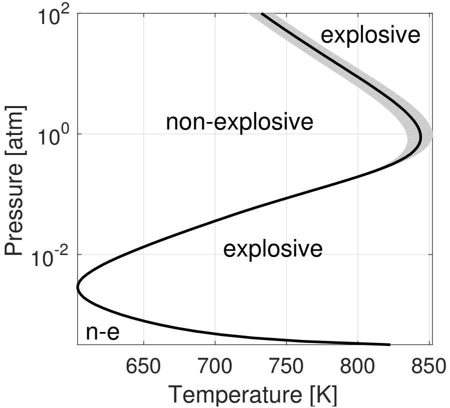

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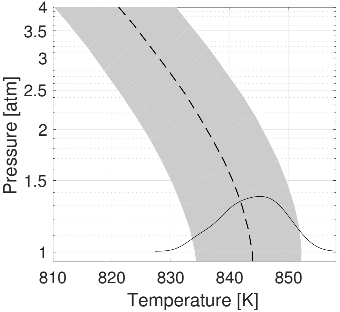
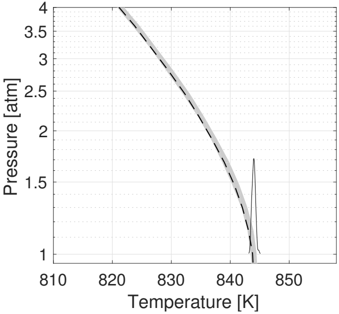
- H_2O_2 decomposition controls the 3rd explosion limit in the H_2-O_2 system
- forward model: homogenous ignition delay
- binary classifier establishes the limit curve within ≈ 0.1 K.

Uncertainty propagation



(a)



(b)

Sampling from uniform space defined by symmetric error bounds predicts large uncertainty in the third limit location, while sampling from the correlated posterior parameter PDF results in much smaller uncertainty

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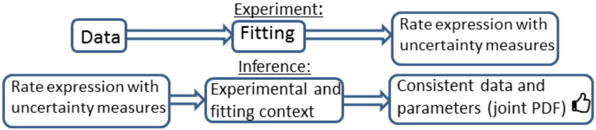
Data combination

Presents a framework for pooling data across experiments for determining consensus rate expresssions.



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