Appendix A: derivation of the likelihood function

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1 Derivation of the Analytical Density of $\hat{\phi}$

Under isothermal conditions, we know that

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

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

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

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

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

Thus, ϕ as a function of $\alpha(t)$ is:

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

We consider now the relationship for the delay time t_d when $\alpha(t_d) = 0.5$:

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

As we saw just above, rearranging for ϕ, the true reaction rate:

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

If r_0 were known perfectly, this would give the exact value of ϕ. However, since r_0 is a random variable following a lognormal distribution with parameters $E(r_0) = \mu$ and $\text{std}(r_0) = \sigma$, we estimate ϕ by replacing r_0 with μ:

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

Dividing $\hat{\phi}$ by ϕ, we find:

$$\frac{\hat{\phi}}{\phi} = \frac{\mu}{r_0},$$

or equivalently:

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

This implies the relationship:

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

Distribution of $\hat{\phi}$

The random variable r_0 is distributed lognormally:

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

where the lognormal parameters are related to the original parameters as:

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

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

Under the transformation $r_0 = \phi \cdot \mu/\hat{\phi}$, the Jacobian is given by:

$$J = \left|\frac{\partial r_0}{\partial \hat{\phi}}\right| = \frac{\phi \cdot \mu}{\hat{\phi}^2}.$$

The density of $\hat{\phi}$ given ϕ is then:

$$f(\hat{\phi} \mid \phi) = f_{r_0}(r_0) \cdot J,$$

or explicitly:

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

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

2 Derivation of the Conditional Density of $\hat{\phi}$ Given E_a

We aim to derive the conditional density $f(\hat{\phi} \mid E_a)$, where E_a represents the activation energy.

Step 1: Relating ϕ to E_a via the Arrhenius Equation

The true reaction rate ϕ is linked to the true activation energy $E_{a,true}$ using the Arrhenius equation:

$$\phi = A_{\text{true}} \cdot \exp\left(-\frac{E_{a,true}}{R \cdot (T + 273.15)}\right),$$

where:

- A_{true} is the true pre-exponential factor,
- R is the universal gas constant,
- T is the temperature in degrees Celsius (°C).

Step 2: Connecting $\hat{\phi}$ and ϕ

From prior work, the estimated reaction rate $\hat{\phi}$ is related to the true reaction rate ϕ through the particle size r_0, as:

$$\hat{\phi} = \phi \cdot \frac{\mu}{r_0},$$

where:

- $r_0 \sim \text{Lognormal}(\mu, \sigma)$, the particle size distribution,
- μ and σ are the mean and standard deviation of r_0, respectively.

The probability density of $\hat{\phi}$ given ϕ is thus:

$$f(\hat{\phi} \mid \phi) = f_{r_0}\left(\frac{\phi \cdot \mu}{\hat{\phi}}\right) \cdot \left|\frac{\partial r_0}{\partial \hat{\phi}}\right|,$$

where $r_0 = \phi \cdot \mu / \hat{\phi}$, and the Jacobian is:

$$\left|\frac{\partial r_0}{\partial \hat{\phi}}\right| = \frac{\phi \cdot \mu}{\hat{\phi}^2}.$$

Step 3: Conditional Density of $\hat{\phi}$ Given E_a

The conditional density $f(\hat{\phi} \mid E_a)$ is obtained by incorporating the relationship between ϕ and E_a:

$$f(\hat{\phi} \mid E_a) = f(\hat{\phi} \mid \phi) \cdot \left|\frac{\partial \phi}{\partial E_a}\right|,$$

where:

$$\frac{\partial \phi}{\partial E_a} = R \cdot (T + 273.15) \cdot \frac{\exp\left(-\frac{E_a}{R \cdot (T+273.15)}\right)}{\phi}.$$

Substituting $f(\hat{\phi} \mid \phi)$ and $\frac{\partial \phi}{\partial E_a}$, we get:

$$f(\hat{\phi} \mid E_a) = f_{r_0}\left(\frac{\phi \cdot \mu}{\hat{\phi}}\right) \cdot \frac{\phi \cdot \mu}{\hat{\phi}^2} \cdot \left|R \cdot (T + 273.15) \cdot \frac{\exp\left(-\frac{E_a}{R \cdot (T+273.15)}\right)}{\phi}\right|.$$

Step 4: Final Expression for $f(\hat{\phi} \mid E_a)$

Combining terms, the conditional density becomes:

$$f(\hat{\phi} \mid E_a) = f_{r_0}\left(\frac{\phi \cdot \mu}{\hat{\phi}}\right) \cdot \frac{\mu \cdot R \cdot (T + 273.15)}{\hat{\phi}^2} \cdot \exp\left(-\frac{E_a}{R \cdot (T + 273.15)}\right),$$

where $f_{r_0}(r)$ is the lognormal density of r_0:

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

with the lognormal parameters:

$$\sigma_{\log} = \sqrt{\ln\left(1 + \left(\frac{\sigma}{\mu}\right)^2\right)}, \quad \mu_{\log} = \ln(\mu) - \frac{\sigma_{\log}^2}{2}.$$