Modeling of Reactive Heterogeneous Uptake in a Flow Reactor

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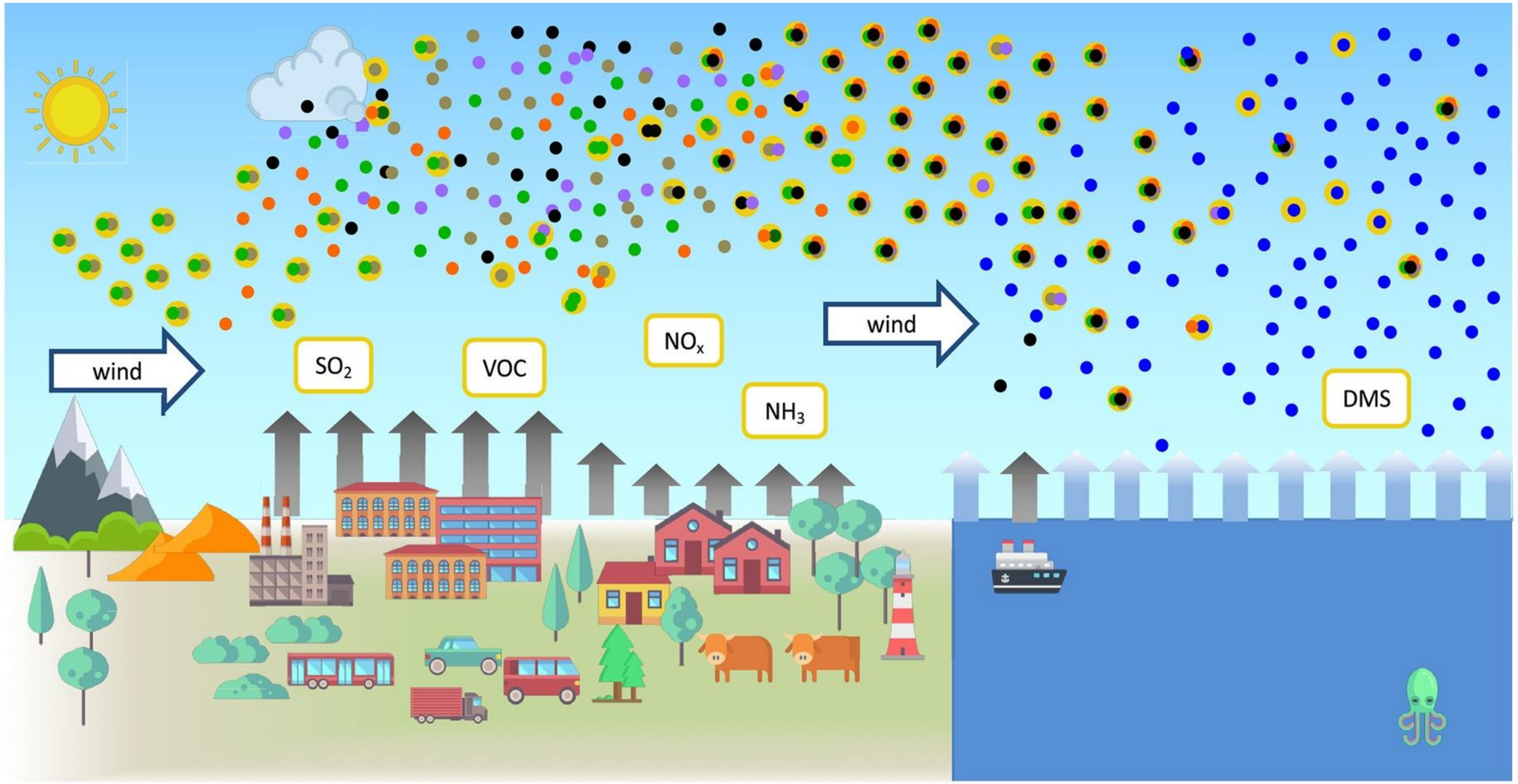
NJIT

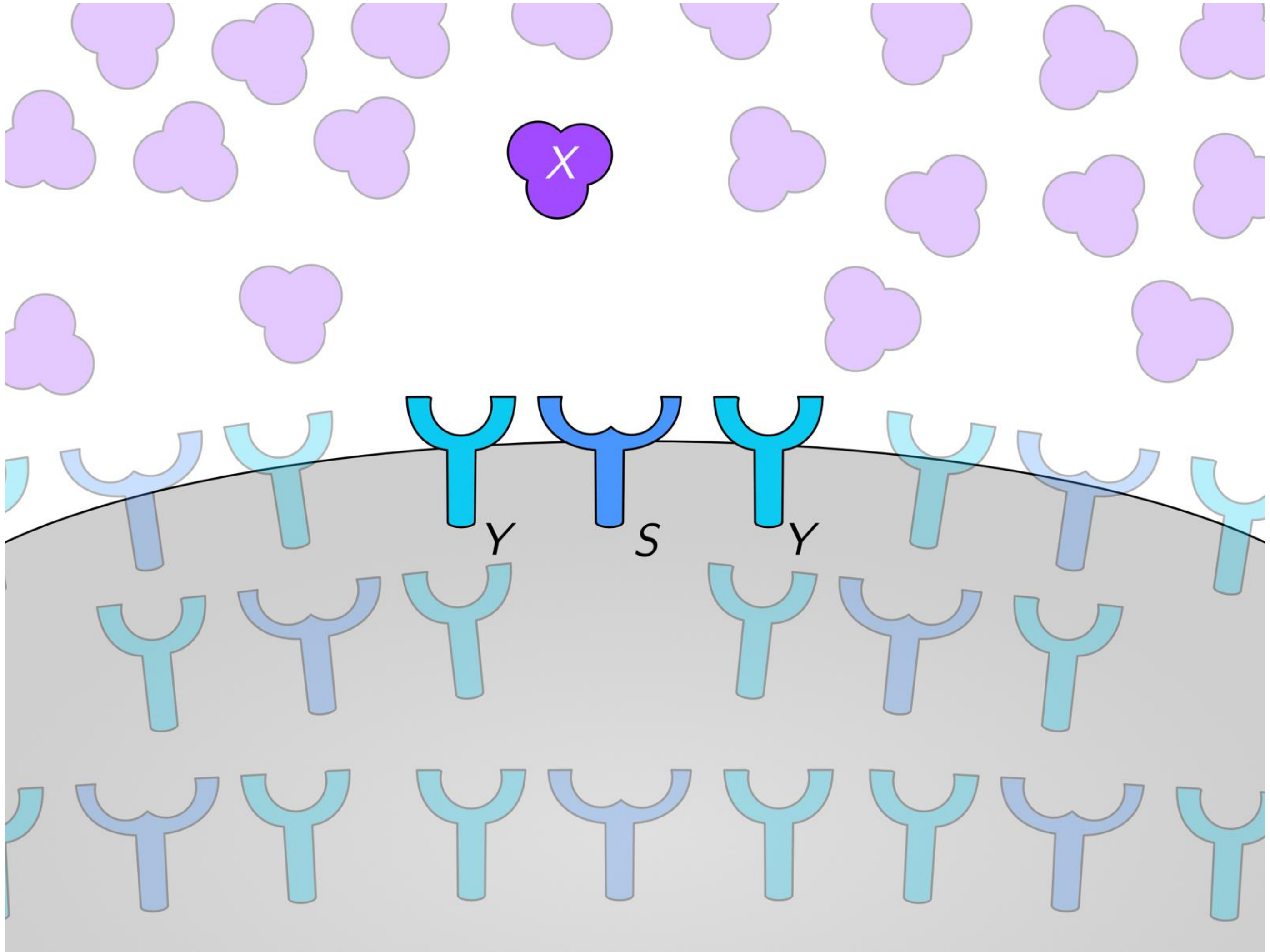
What are aerosols?

- Suspension of liquid or solid particles
- 1 nm – 100 μm
- Impact:
  - Climate
  - Health
  - Role in biological systems
- <u>Aerosols transform during their lifetime in the atmosphere</u>



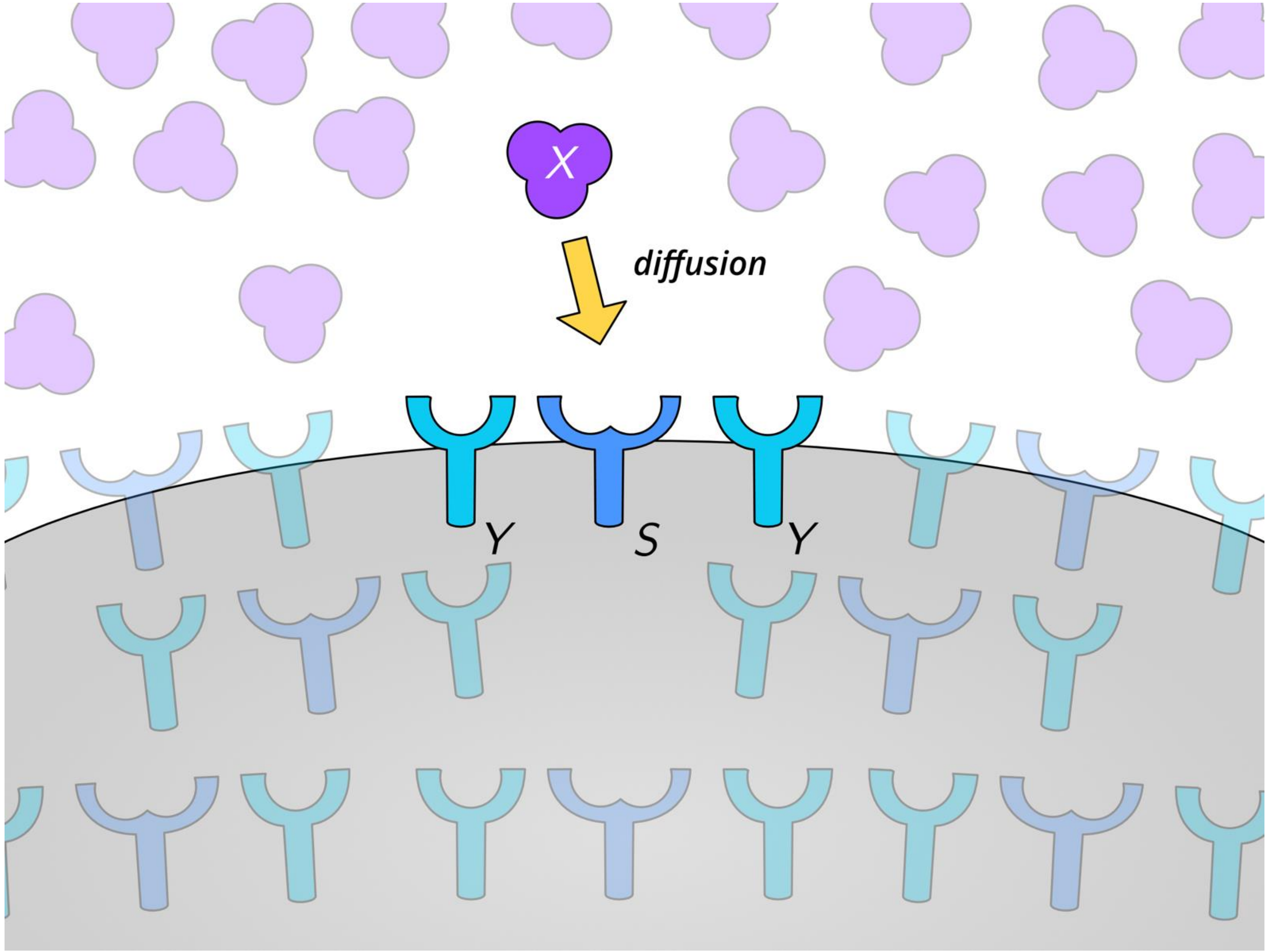
Riemer, N., Ault, A. P., West, M., Craig, R. L., & Curtis, J. H. (2019). Aerosol mixing state: Measurements, modeling, and impacts. *Reviews of Geophysics*, *57*(2), 187-249.

Surface processing of aerosols



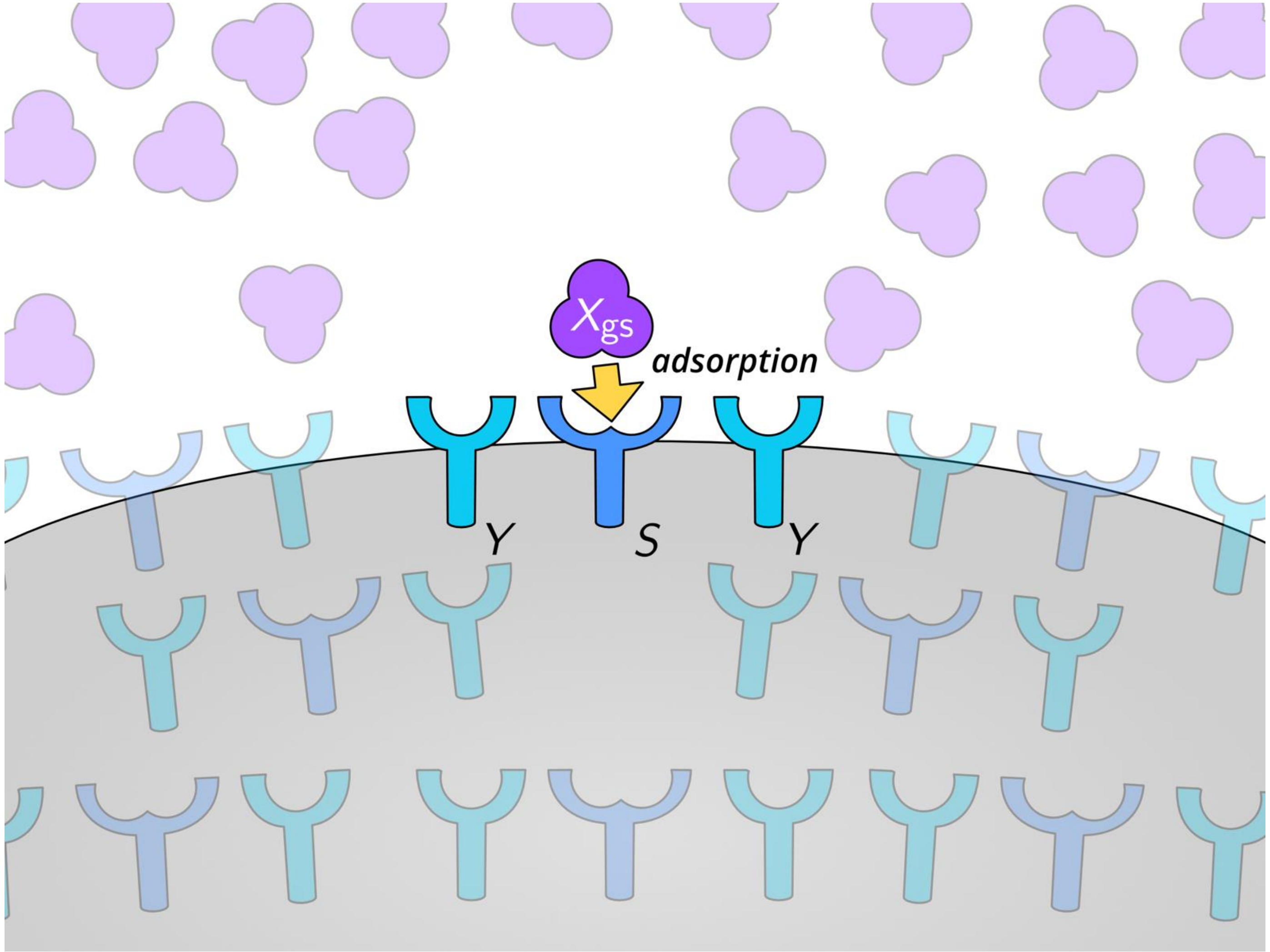
Surface processing of aerosols

$$\mathrm{X} \underset{}{\overset{k_{\mathrm{diff}}}{\rightleftharpoons}} \mathrm{X_{gs}}$$



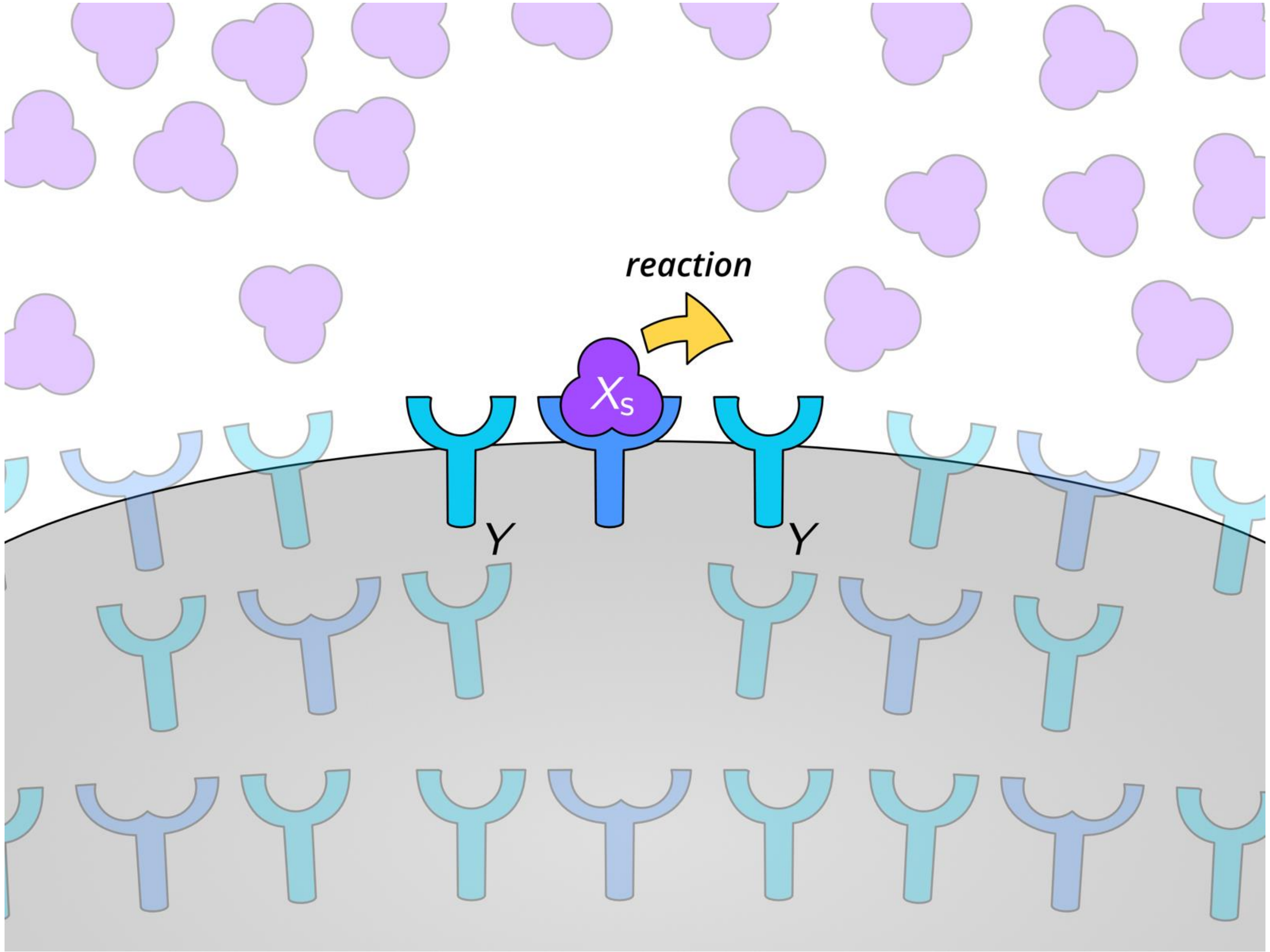
Surface processing of aerosols

$$\mathrm{X_{gs}} + \mathrm{S} \underset{k_{\mathrm{des}}}{\overset{k_{\mathrm{ads}}}{\rightleftharpoons}} \mathrm{X_s}$$



Surface processing of aerosols

$$X_s + Y \longrightarrow P + S$$



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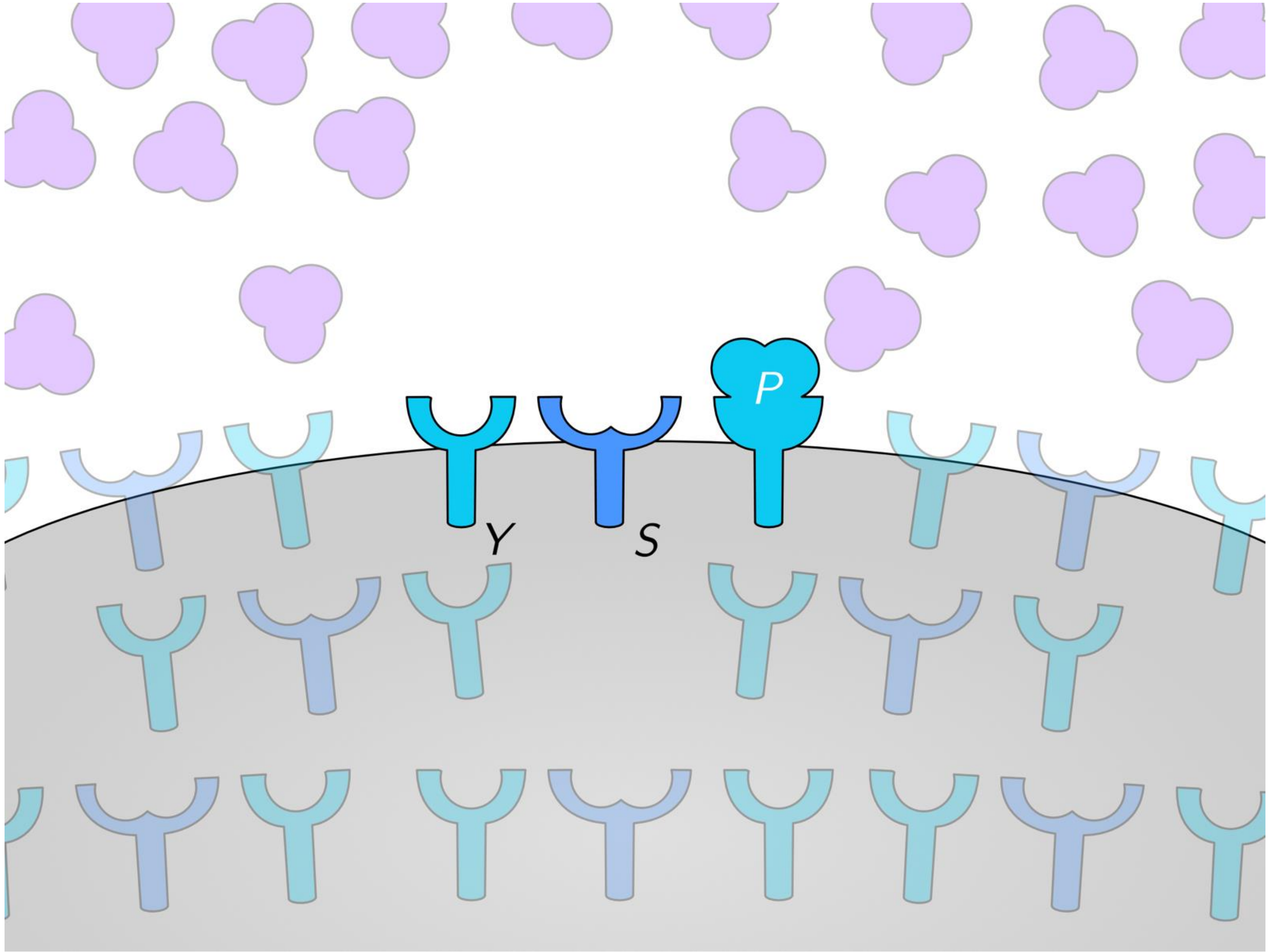


Langmuir-Hinshelwood mechanism

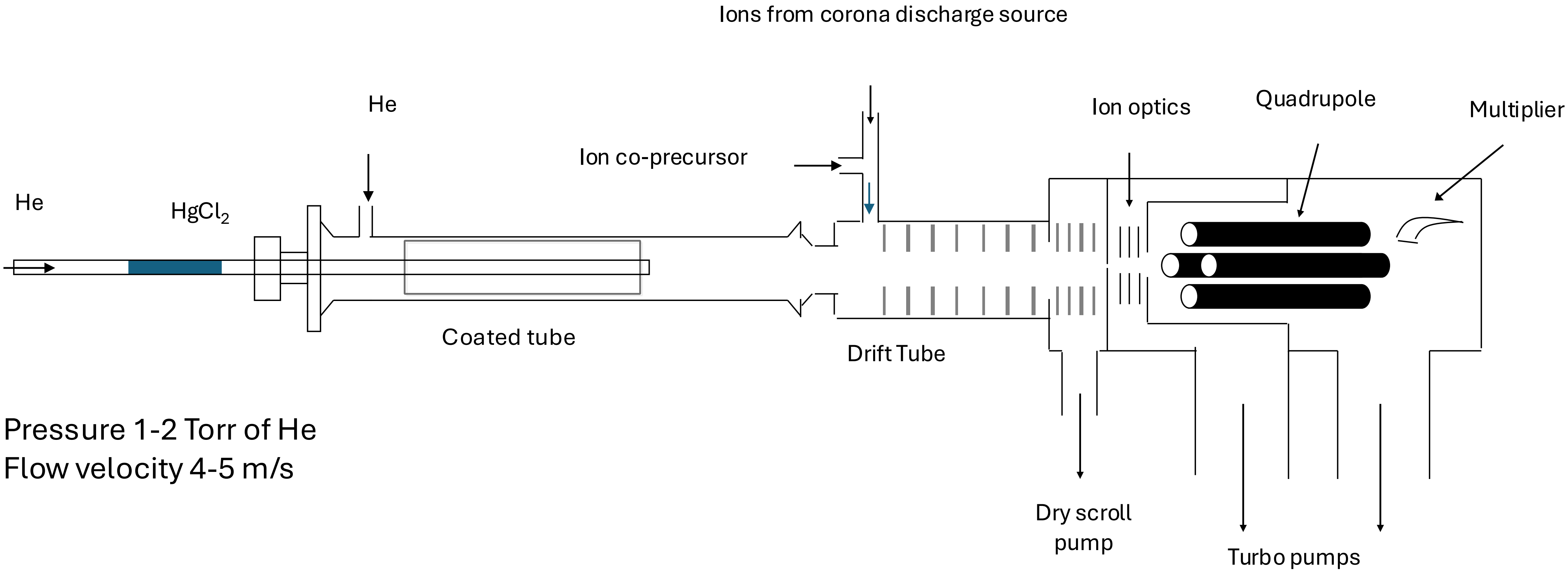
- Examples: ozone, NO_2, mercuric compounds
- Initial rate generally limited by the number of adsorption sites, S

$$\mathrm{X} \underset{}{\overset{k_{\mathrm{diff}}}{\rightleftharpoons}} \mathrm{X_{gs}}$$

$$\mathrm{X_{gs}} + \mathrm{S} \underset{k_{\mathrm{des}}}{\overset{k_{\mathrm{ads}}}{\rightleftharpoons}} \mathrm{X_s}$$

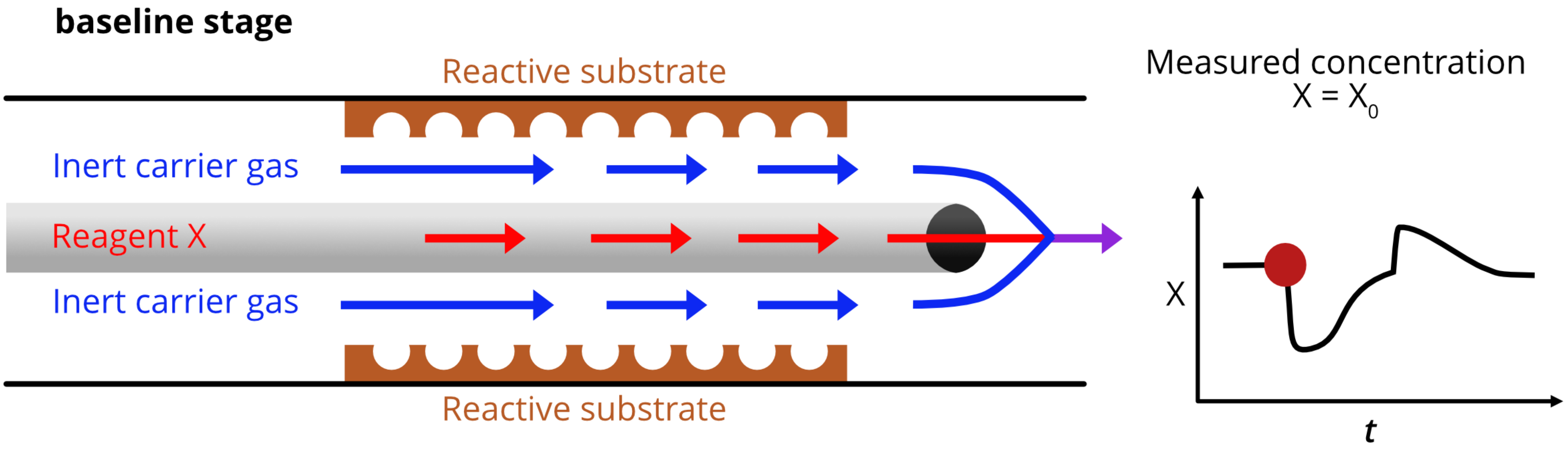
$$\mathrm{X_s} + \mathrm{Y} \longrightarrow \mathrm{P} + \mathrm{S}$$

Experimental setup

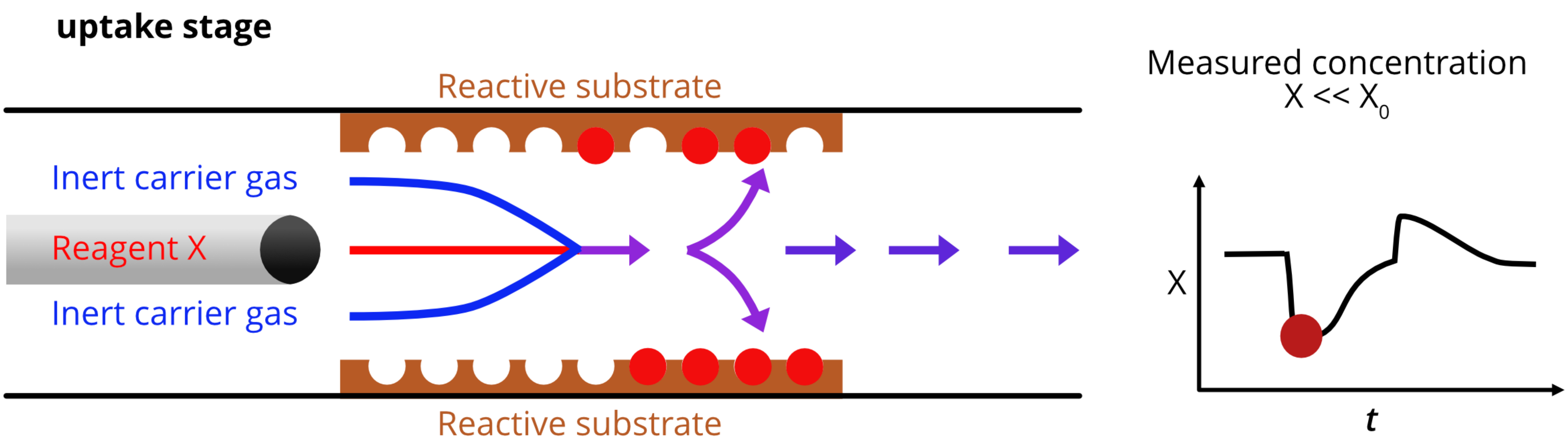


Pressure 1-2 Torr of He
Flow velocity 4-5 m/s

Experimental workflow

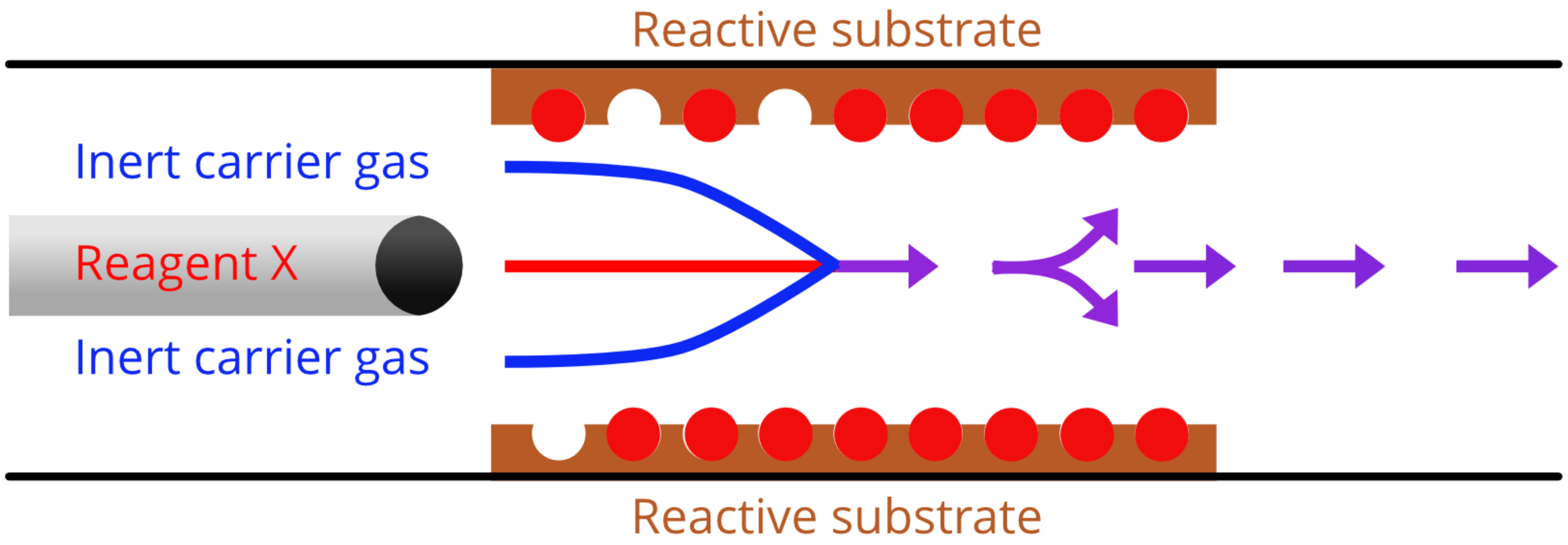


Experimental workflow

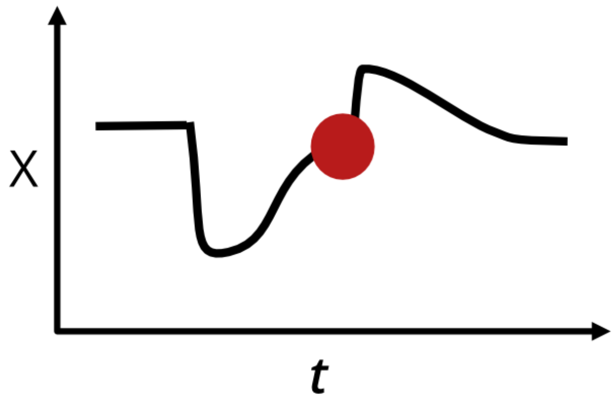


Experimental workflow

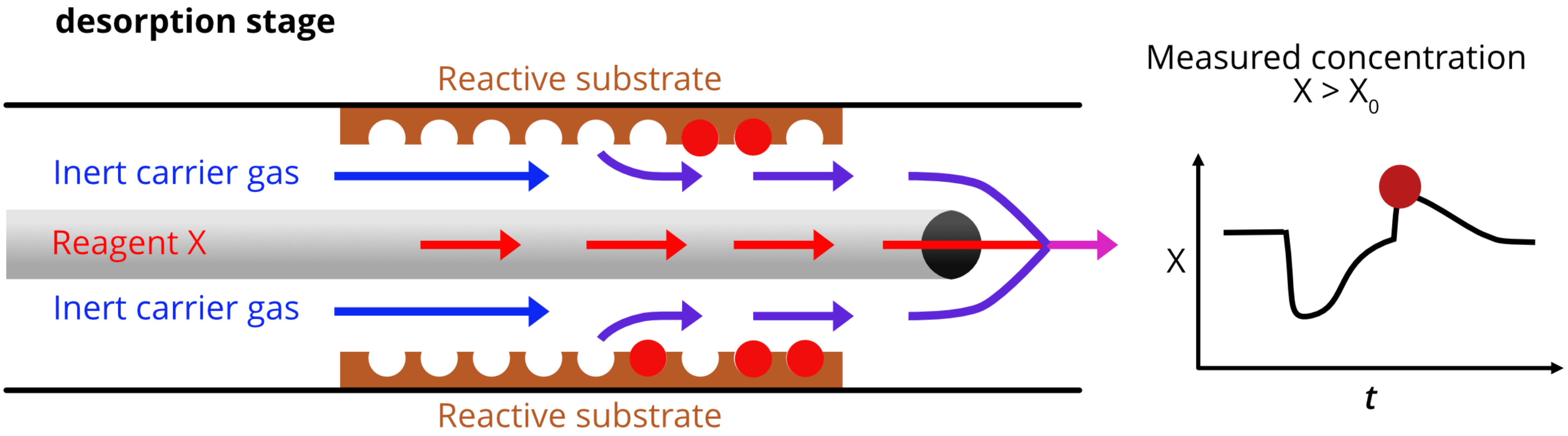
uptake stage - surface saturation



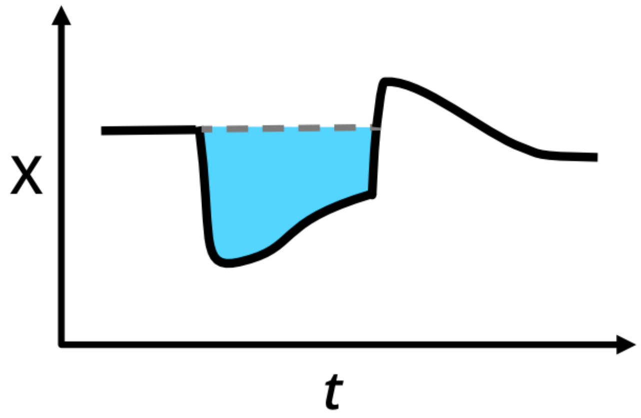
Measured concentration
$X < X_0$



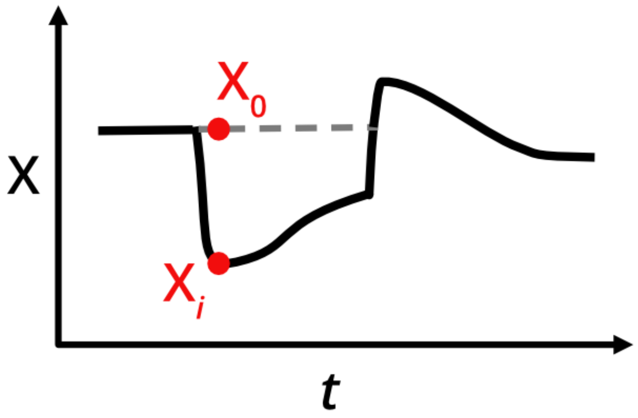
Experimental workflow



Processing of experimental data



Surface capacity, [mol cm^{-2}]

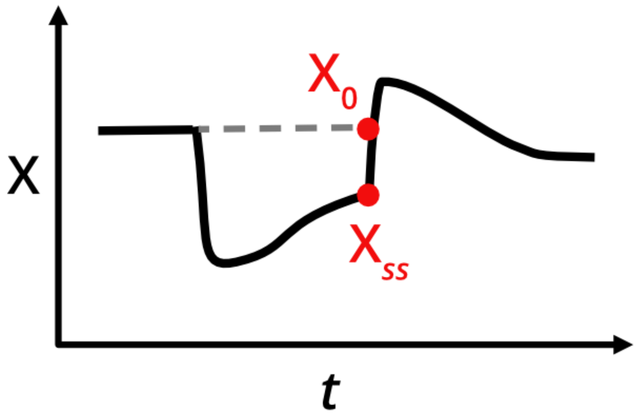


Initial uptake coefficient, γ_i

$$k_{\text{obs},i} = \frac{u}{L}\ln\frac{X_0}{X_i}$$

$$\gamma_i = \frac{2rk_{\text{obs,i}}}{\omega}$$

$$\tau \propto \frac{1}{\gamma_i}$$



Steady state uptake coefficient, γ_{ss}

$$k_{\text{obs},ss} = \frac{u}{L}\ln\frac{X_0}{X_{ss}}$$

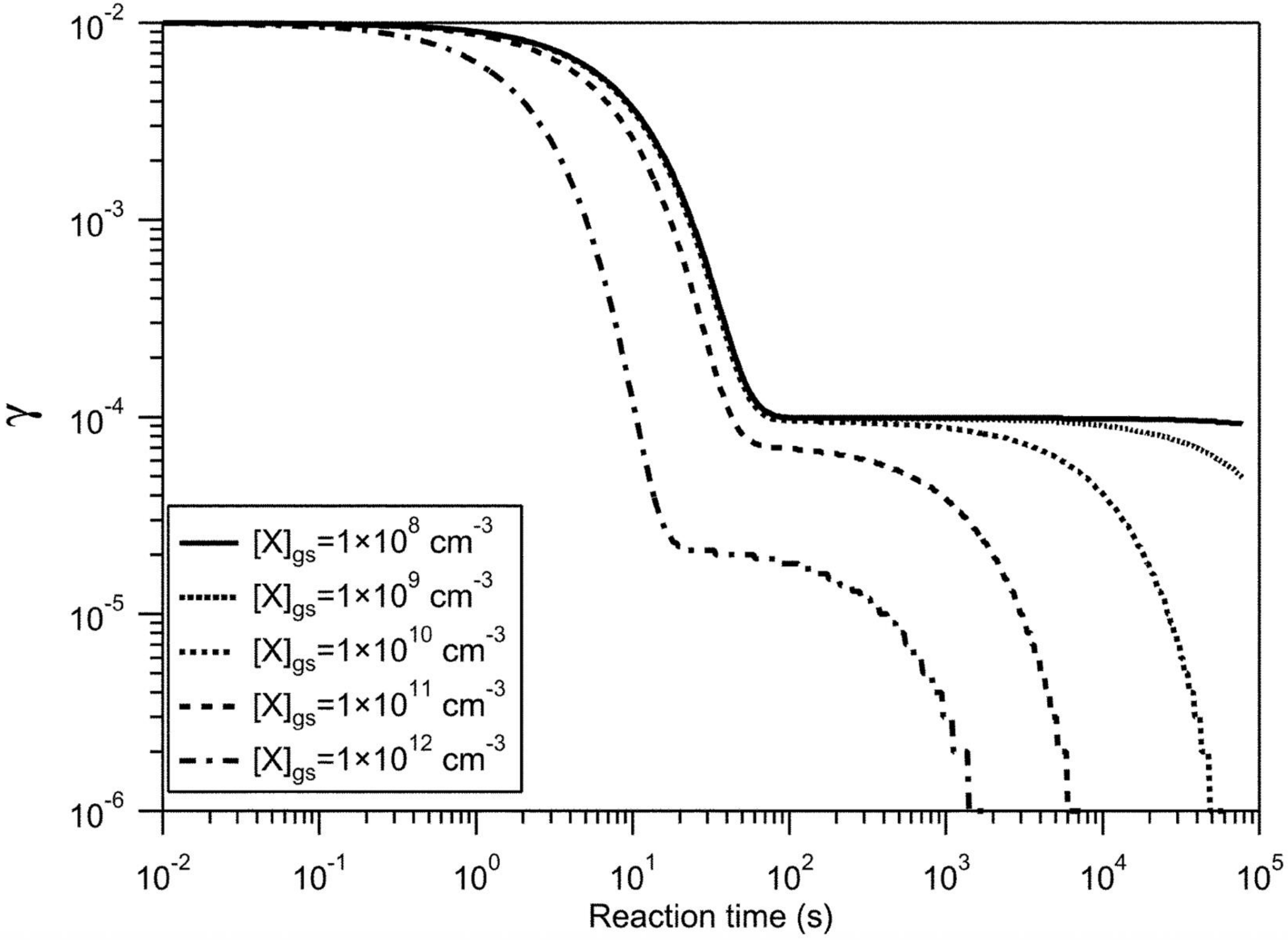
$$\gamma_{ss} = \frac{2rk_{\text{obs,i}}}{\omega}$$

$$\boldsymbol{\gamma \equiv \frac{\text{uptake collisions}}{\text{total collisions}}}$$

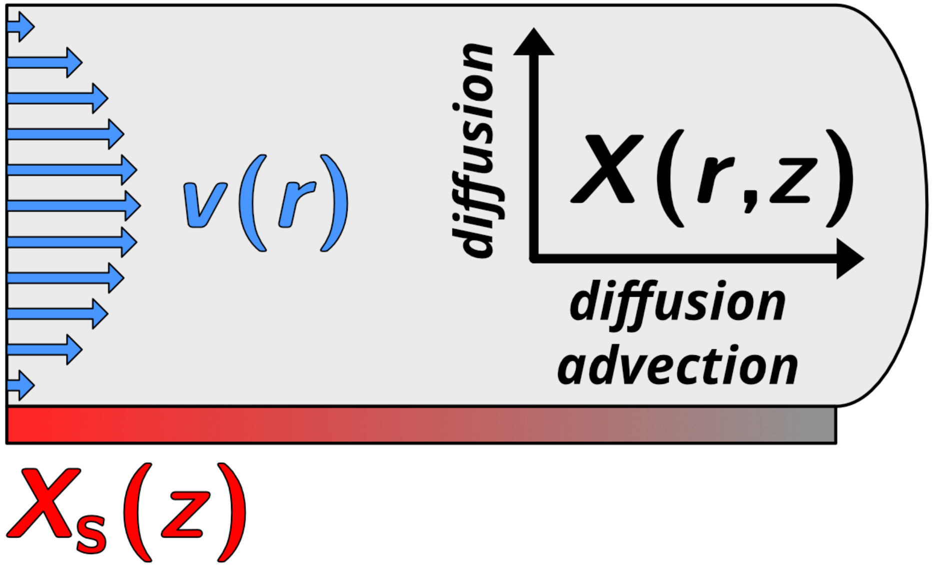
Previous work

- Model by Ammann et al. 2002:
  - For surface chemistry and uptake coefficients
  - No gas-phase transport
- <u>Our goal</u>: develop a model for post-processing experimental data

Model-predicted uptake coefficient



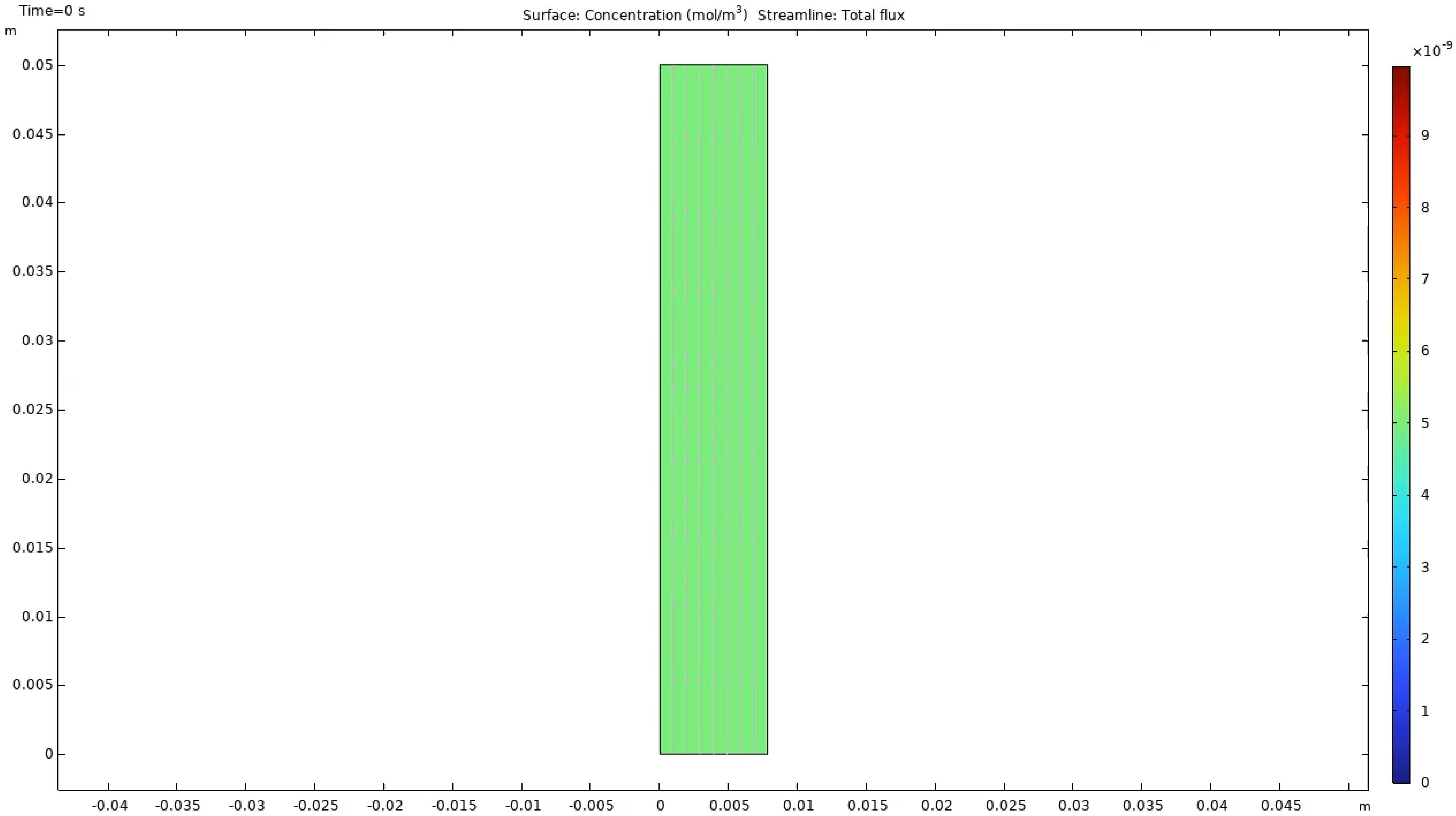
2D model



Resolves:

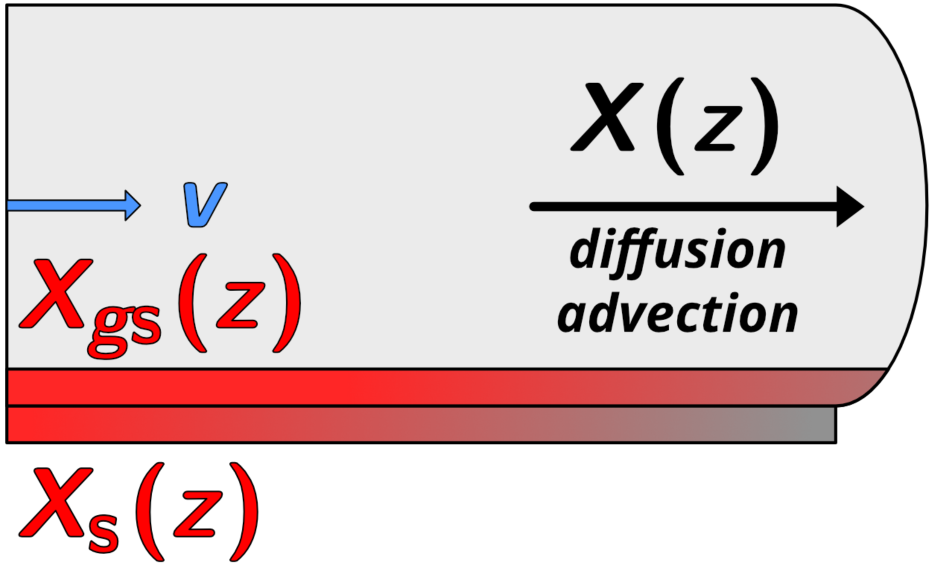
- ✅ **Radial velocity profile**
- ✅ **Radial and axial diffusion**
- ✅ **Axial profile of surface species**

$$\underbrace{\frac{\partial X}{\partial t}}_{\text{Time dependence}} + \underbrace{2v\left[1 - \frac{r^2}{R^2}\right]\frac{\partial X}{\partial z}}_{\text{Advection}} = \underbrace{D_i \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial X}{\partial r}\right)}_{\text{Radial diffusion}} + \underbrace{D_i \frac{\partial^2 X}{\partial z^2}}_{\text{Axial diffusion}}$$



Time=0 s
Surface: Concentration (mol/m^3) Streamline: Total flux
m
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
-0.04 -0.035 -0.03 -0.025 -0.02 -0.015 -0.01 -0.005 0 0.005 0.01 0.015 0.02 0.025 0.03 0.035 0.04 0.045
m
×10^{-9}
9
8
7
6
5
4
3
2
1
0

1D model



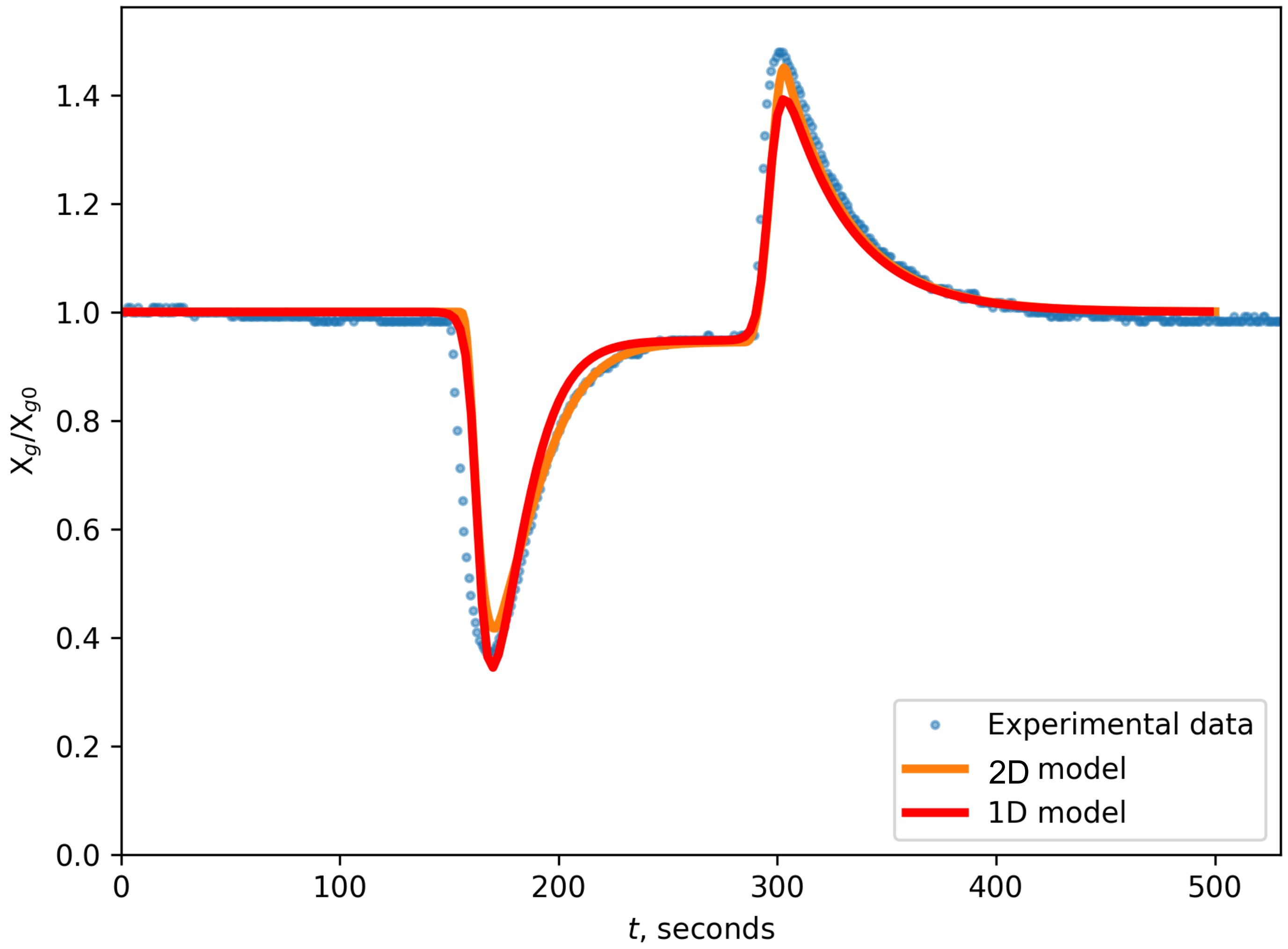
Resolves:

- ✓ Axial diffusion
- ✓ Axial profile of surface species
- – Radial diffusion
- ✗ Radial velocity profile

$$\underbrace{\frac{\partial X}{\partial t}}_{\text{Time dependence}} + \underbrace{v\frac{\partial X}{\partial z}}_{\text{Advection}} = \underbrace{D_i \frac{\partial^2 X}{\partial z^2}}_{\text{Axial diffusion}} - \underbrace{k_{\text{diff}}(X - X_{\text{gs}})}_{\text{Radial diffusion}}$$

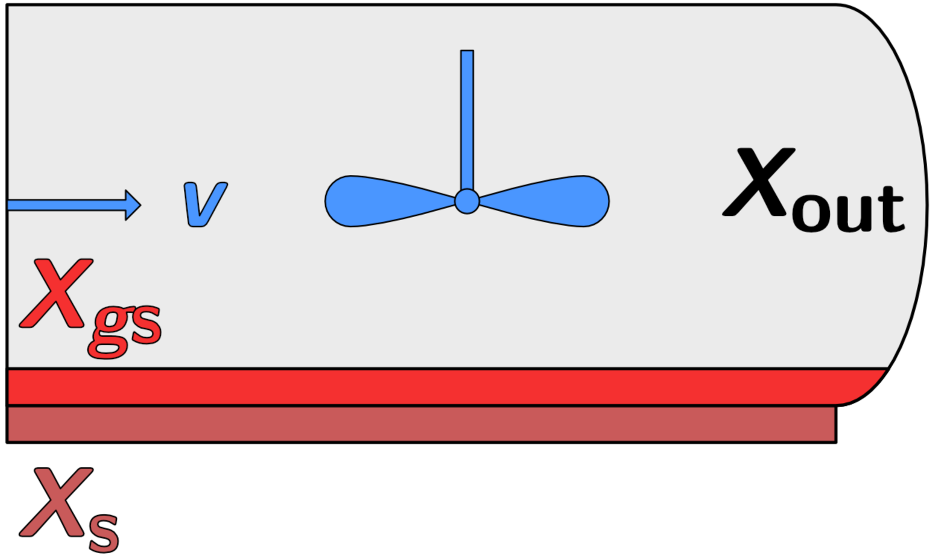
$$\frac{dX_{\text{gs}}}{dt} = k_{\text{diff}}(X - X_{\text{gs}}) - r_{\text{ads}}(X_{\text{gs}}, X_{\text{s}}, P)$$

Appropriate when diffusion is much faster than advection



X_g/X_{g0}
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
t, seconds
Experimental data
2D model
1D model

CSTR model



Resolves:

- Radial diffusion (partially)
- ✗ Axial diffusion
- ✗ Axial profile of surface species
- ✗ Radial velocity profile

$$\underbrace{\frac{dX}{dt}}_{\text{Time dependence}} = \underbrace{\frac{F}{V}(X_{\mathrm{in}} - X)}_{\text{Inflow / outflow}} - \underbrace{k_{\mathrm{diff}}(X - X_{\mathrm{gs}})}_{\text{Radial diffusion}}$$

Appropriate when the reactor is short relative to its width

$$\frac{dX_{\mathrm{gs}}}{dt} = k_{\mathrm{diff}}(X - X_{\mathrm{gs}}) - r_{\mathrm{ads}}(X_{\mathrm{gs}}, X_{\mathrm{s}}, P)$$

Fitting data to CSTR model

4 states

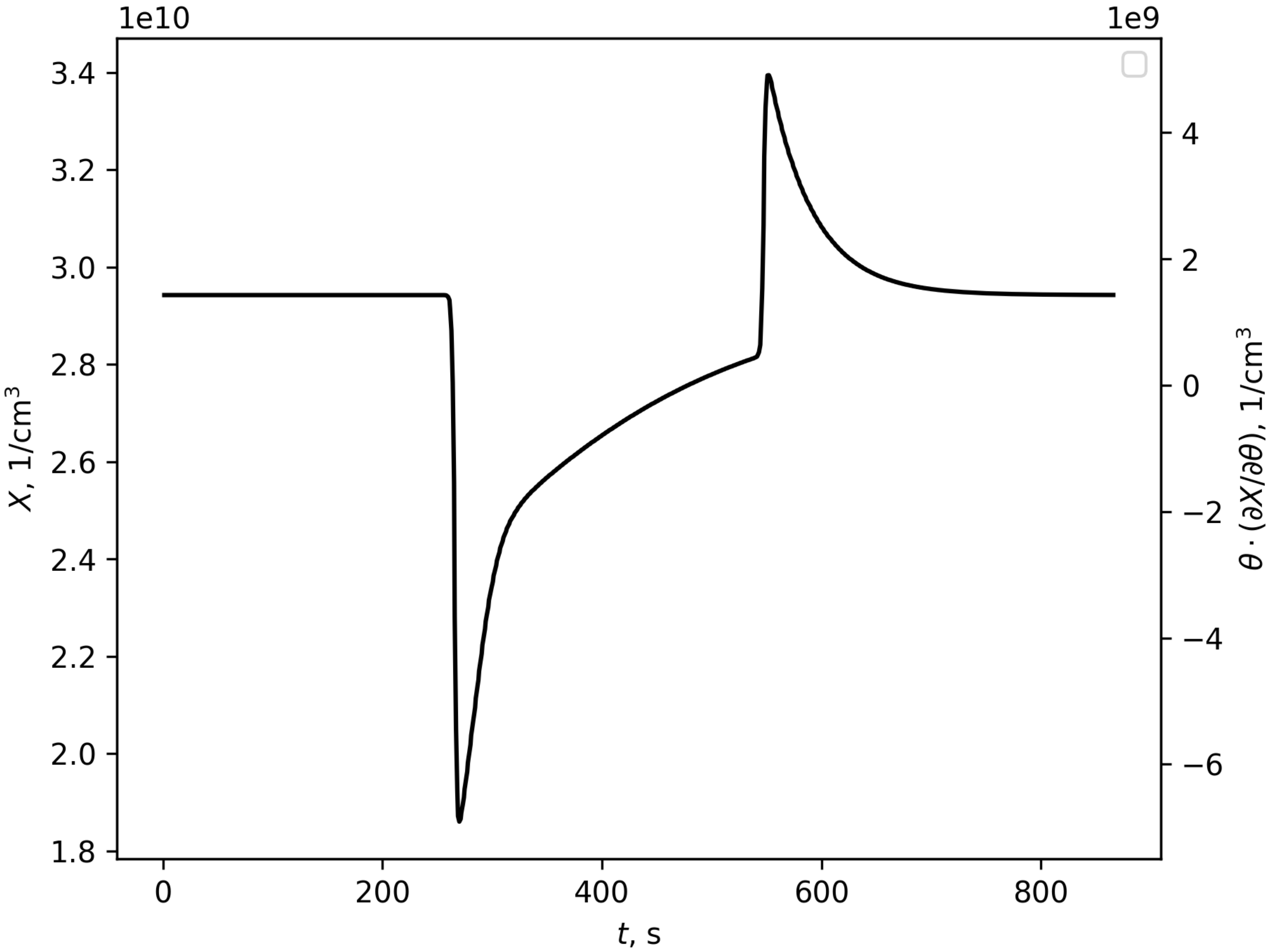
$$\begin{cases} \dfrac{dX}{dt} = \dfrac{F}{V}(X_{\text{in}} - X) - k_{\text{diff}}(X - X_{\text{gs}}) \\ \dfrac{dX_{\text{gs}}}{dt} = k_{\text{diff}}(X - X_{\text{gs}}) - \dfrac{2}{R}k_{\text{ads}}X_{\text{gs}}(S_{\text{tot}} - X_{\text{s}}) + k_{\text{des}}X_{\text{s}} \\ \dfrac{dX_{\text{s}}}{dt} = k_{\text{ads}}X_{\text{gs}}(S_{\text{tot}} - X_{\text{s}}) - \dfrac{R}{2}k_{\text{des}}X_{\text{s}} - k_{\text{rxn}}X_{\text{s}}(Y_{\text{tot}} - P) \\ \dfrac{dP}{dt} = k_{\text{rxn}}X_{\text{s}}(Y_{\text{tot}} - P) \end{cases}$$

$$\underbrace{k_{\text{ads}}, k_{\text{des}}, k_{\text{rxn}}, S_{\text{tot}}, Y_{\text{tot}}}_{\text{5 parameters}}$$

$$\Rightarrow \begin{bmatrix} \dfrac{\partial}{\partial k_{\text{ads}}} \\ \dfrac{\partial}{\partial k_{\text{des}}} \\ \dfrac{\partial}{\partial k_{\text{rxn}}} \\ \dfrac{\partial}{\partial S_{\text{tot}}} \\ \dfrac{\partial}{\partial Y_{\text{tot}}} \end{bmatrix} \begin{bmatrix} X & X_{\text{gs}} & X_{\text{s}} & P \end{bmatrix}$$

20 sensitivity ODEs

Sensitivities



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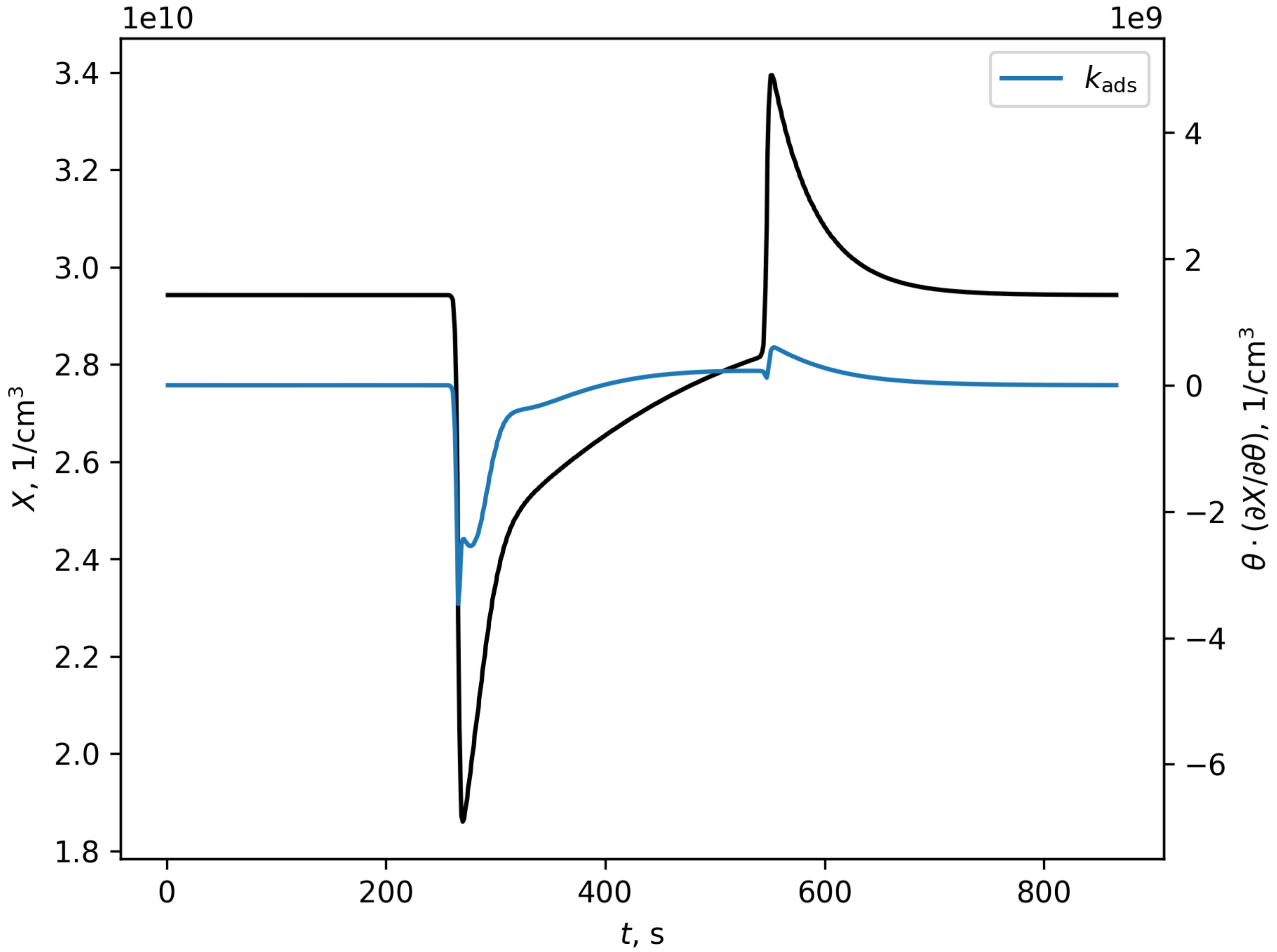
$$\mathrm{X_{gs}} + \mathrm{S} \underset{k_{\mathrm{des}}}{\overset{k_{\mathrm{ads}}}{\rightleftharpoons}} \mathrm{X_s}$$

$$\mathrm{X_s} + \mathrm{Y} \longrightarrow \mathrm{P} + \mathrm{S}$$

Sensitivities

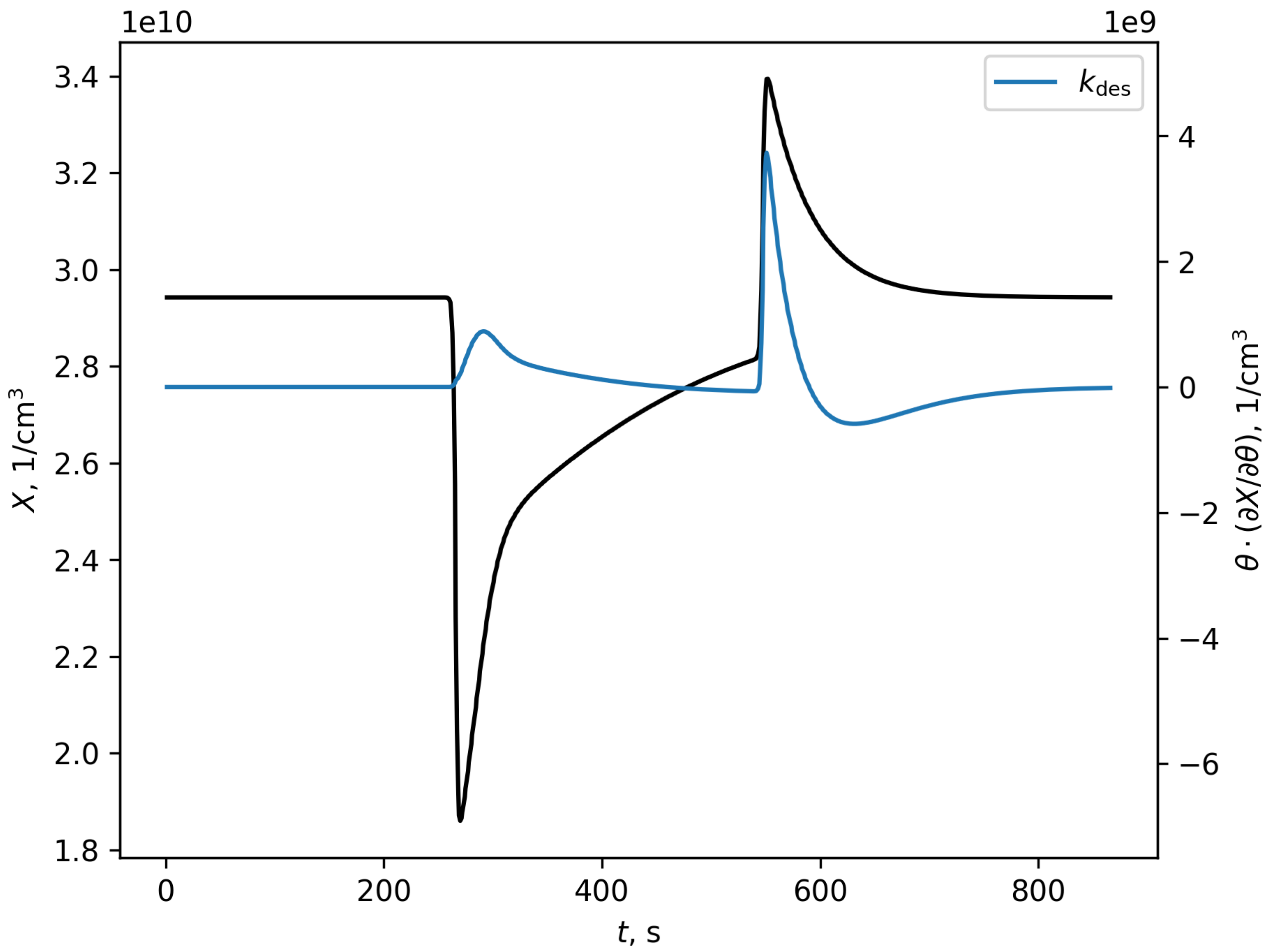


$$\mathrm{X} \xrightleftharpoons{k_{\mathrm{diff}}} \mathrm{X_{gs}}$$

$$\mathrm{X_{gs}} + \mathrm{S} \xrightleftharpoons[k_{\mathrm{des}}]{k_{\mathrm{ads}}} \mathrm{X_s}$$

$$\mathrm{X_s} + \mathrm{Y} \longrightarrow \mathrm{P} + \mathrm{S}$$

Sensitivities



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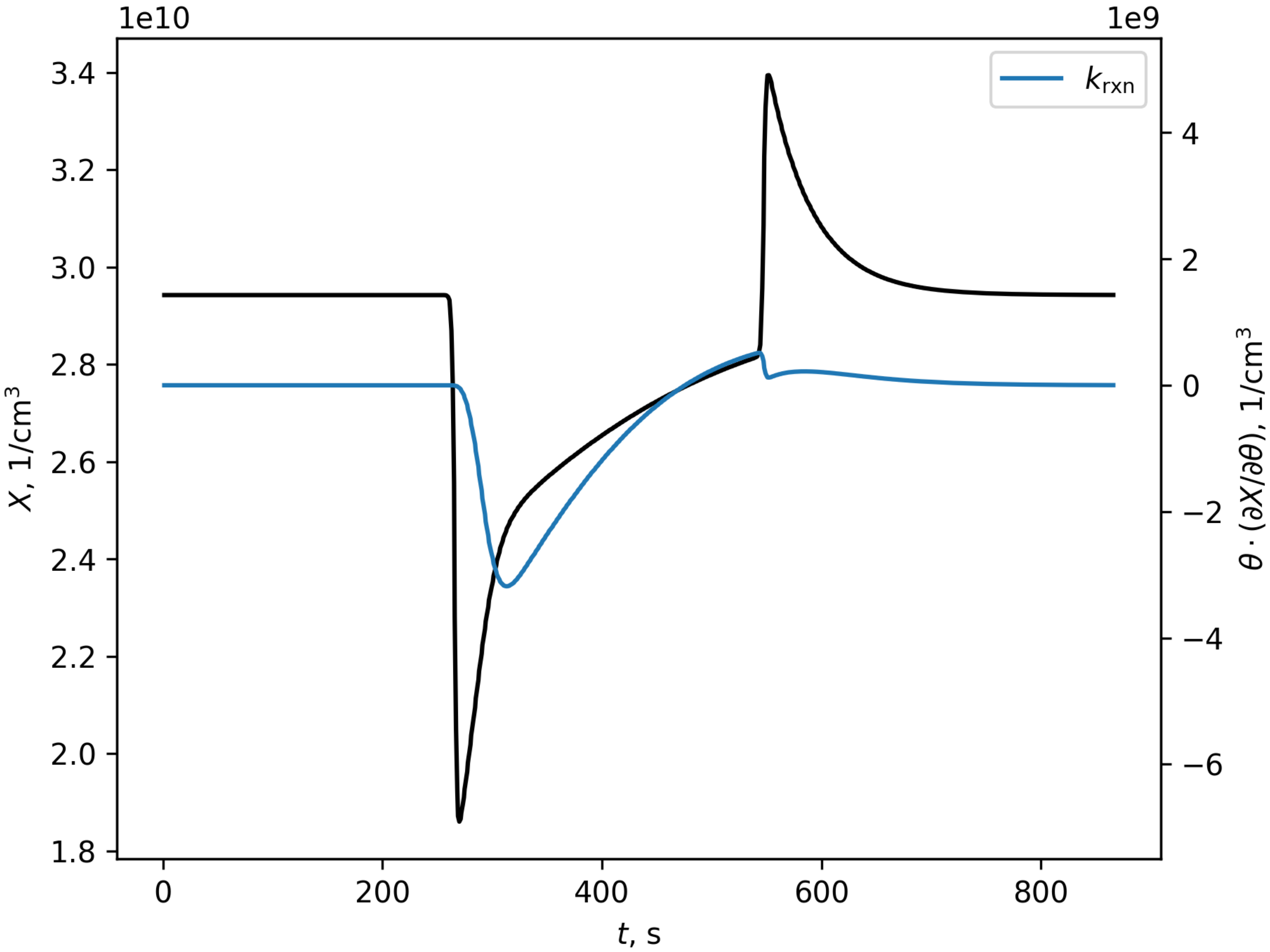

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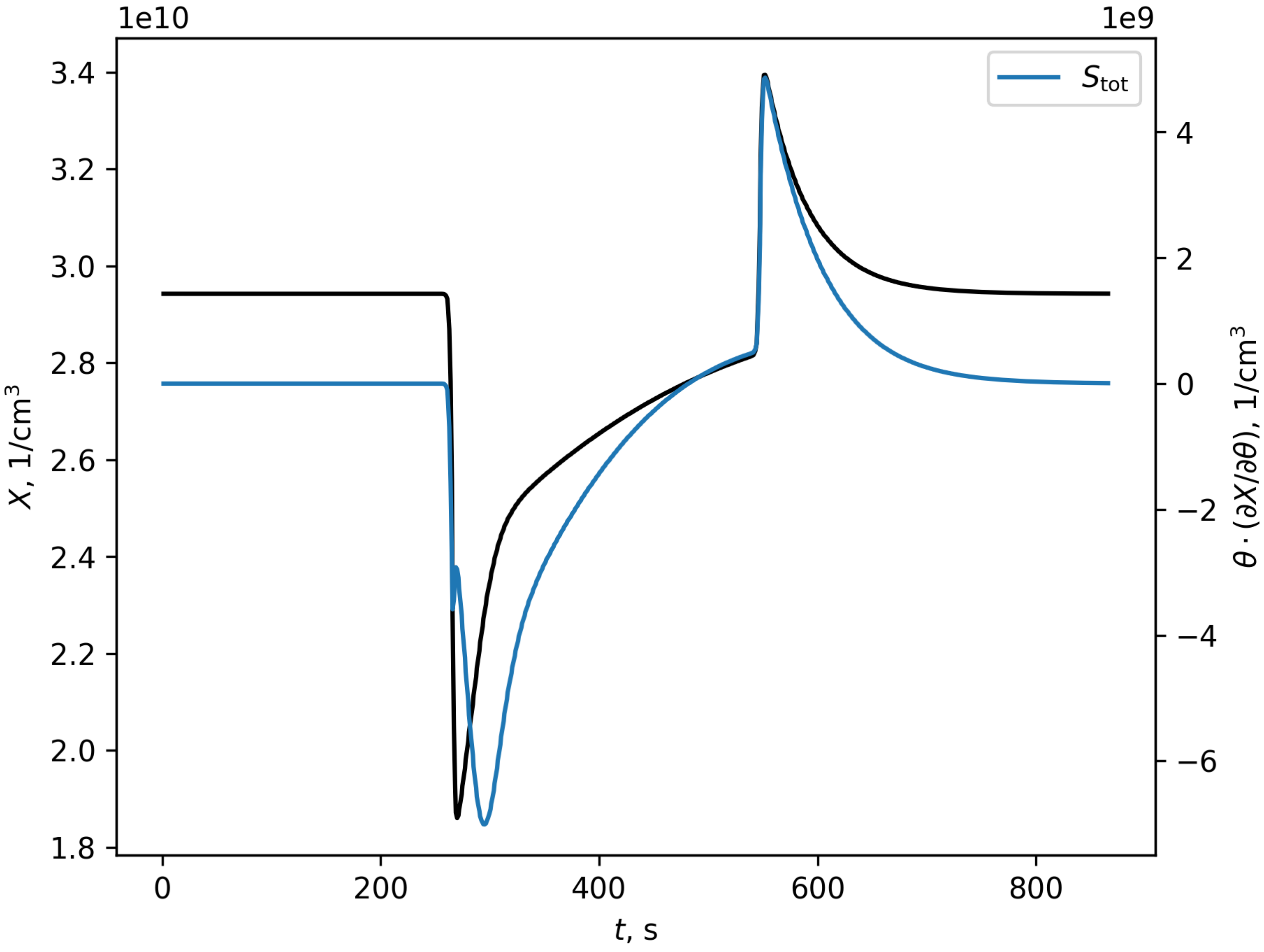
Sensitivities



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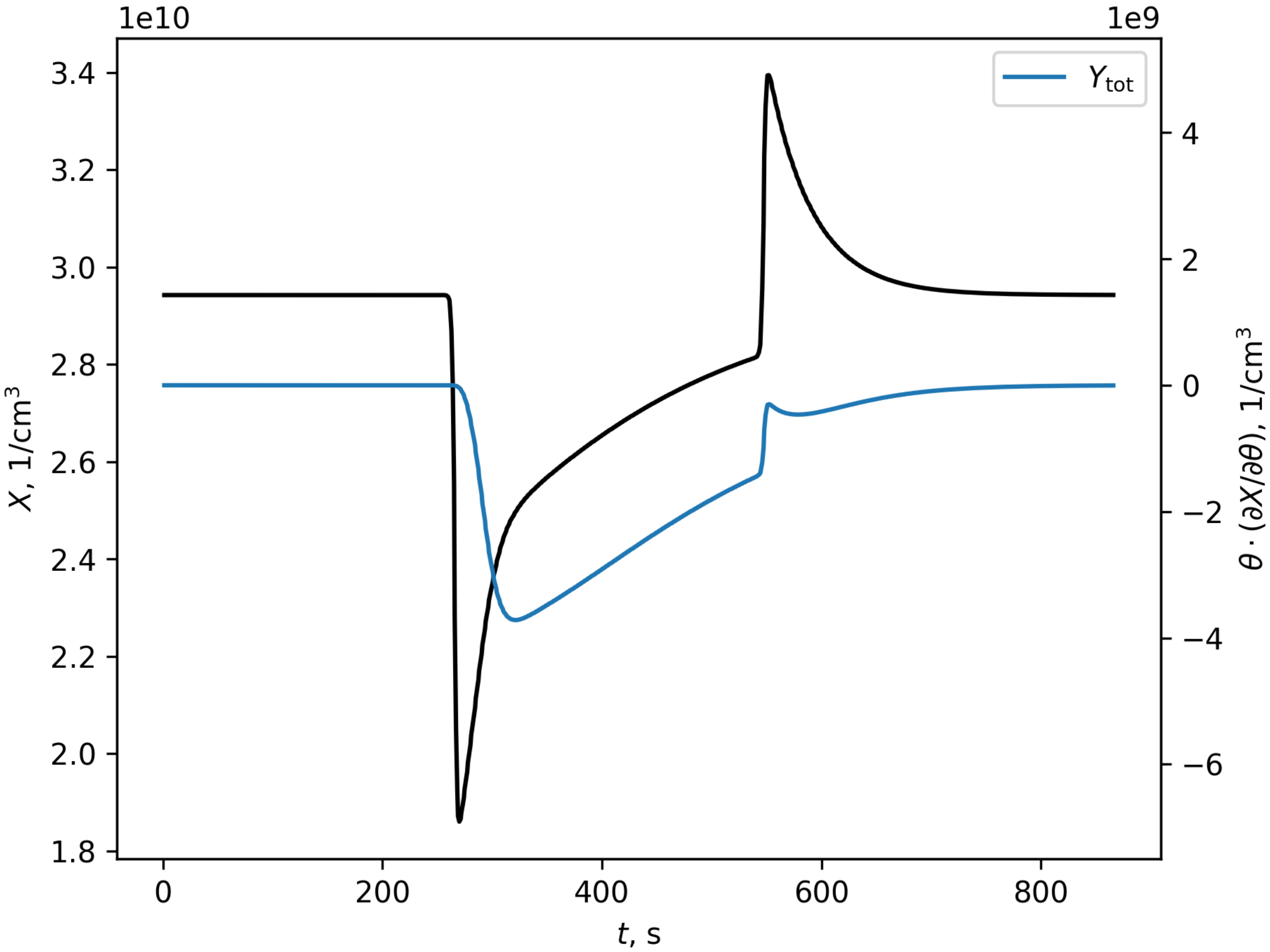

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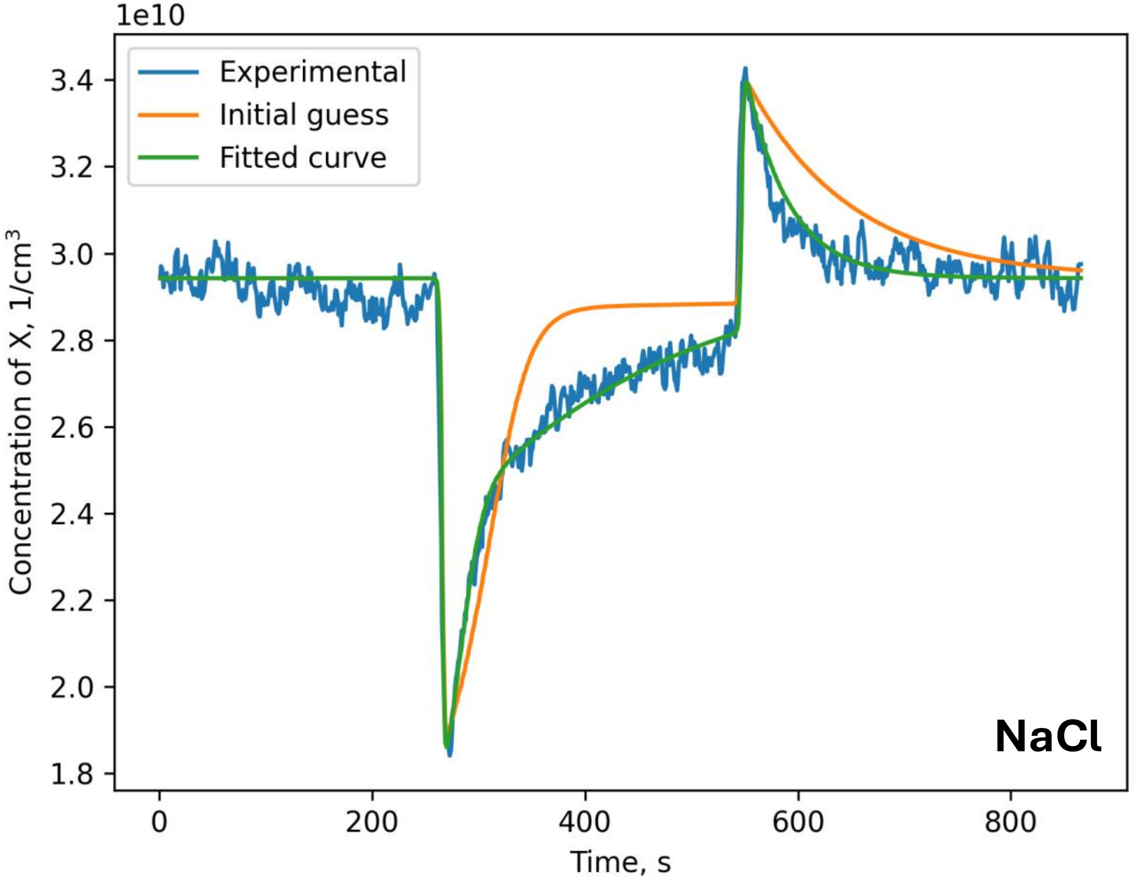
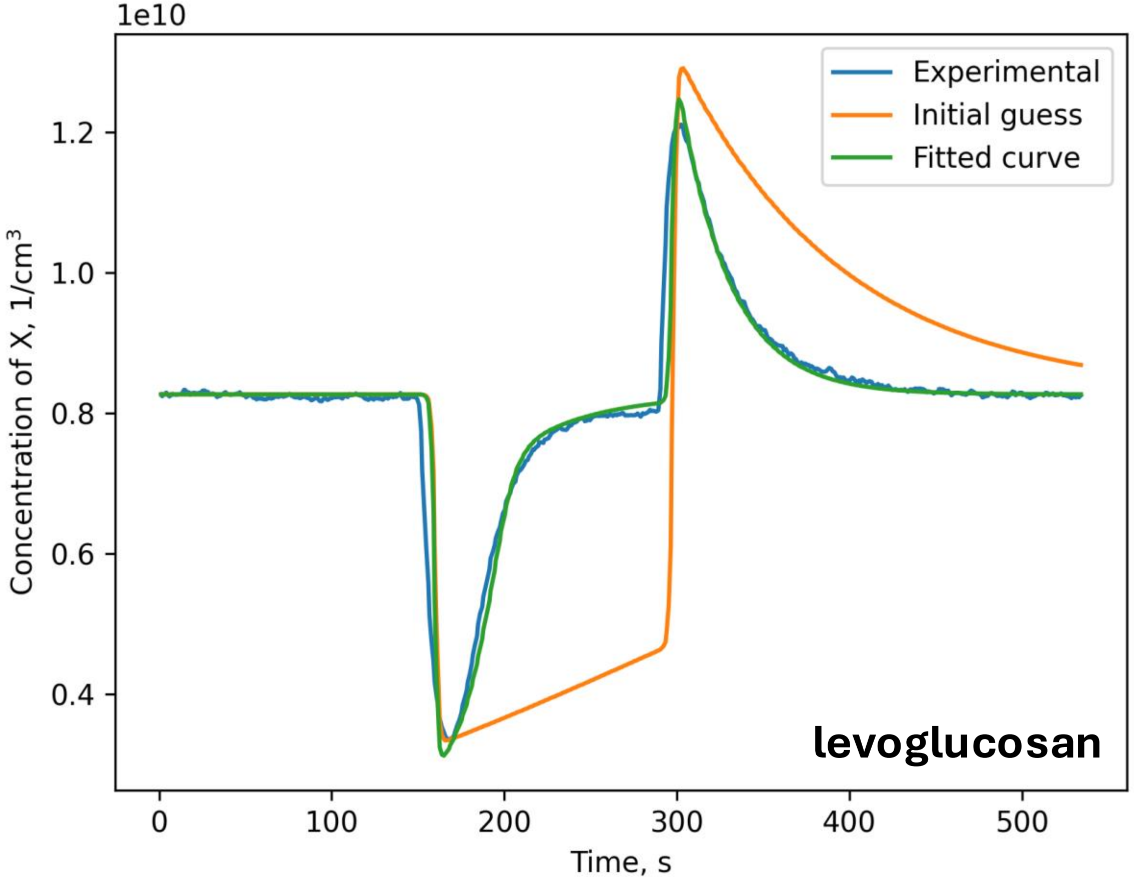
Example fits





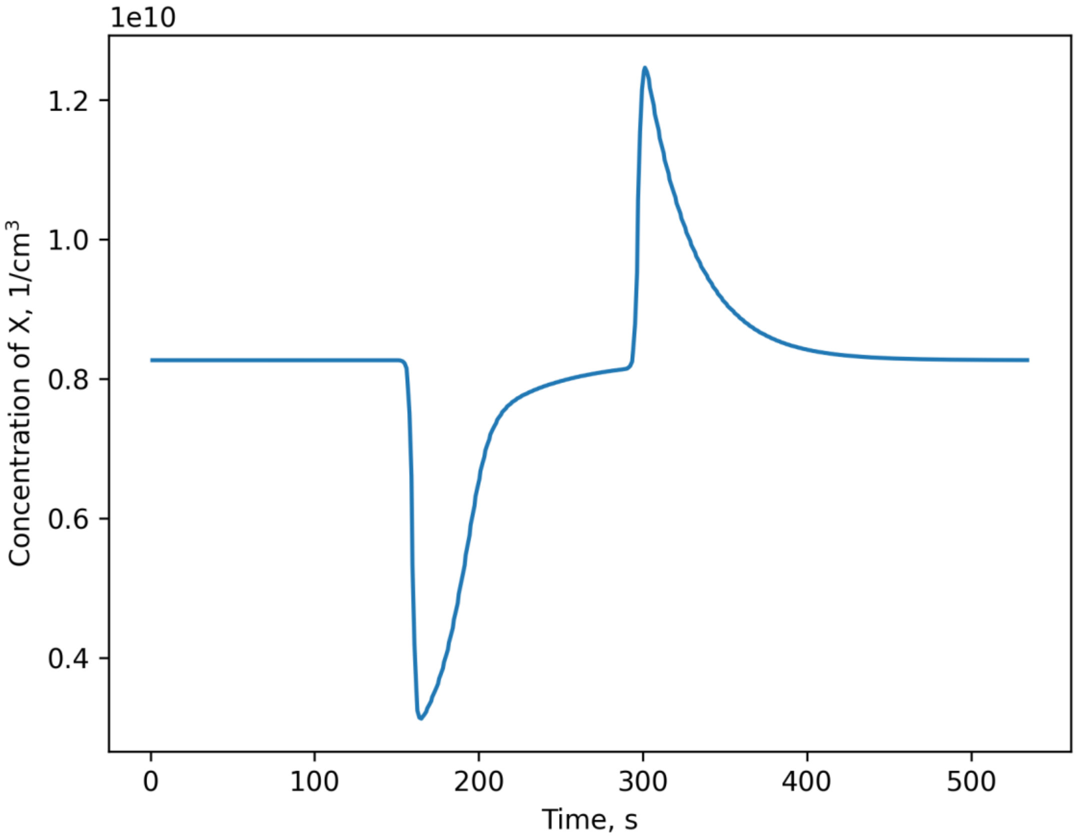
k_{ads}, cm^3s^{-1}	k_{des}, $cm^{-1}s^{-1}$	k_{rxn}, cm^2s^{-1}
2.62e-12	2.36e-02	1.37e-17

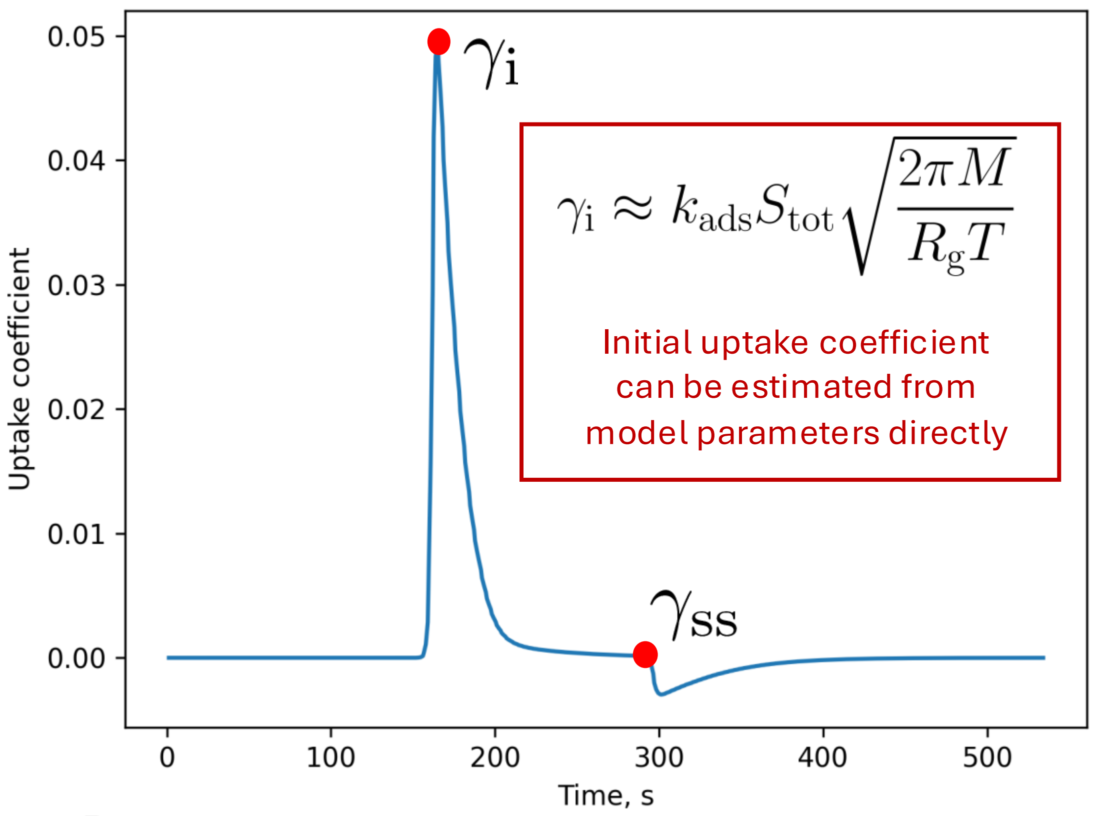
S_{tot}, cm^{-2}	Y_{tot}, cm^{-2}
5.83e13	9.65e13

k_{ads}, cm^3s^{-1}	k_{des}, $cm^{-1}s^{-1}$	k_{rxn}, cm^2s^{-1}
4.57e-11	8.62e-02	3.89e-15

S_{tot}, cm^{-2}	Y_{tot}, cm^{-2}
6.16e12	2.27e12

Uptake coefficients





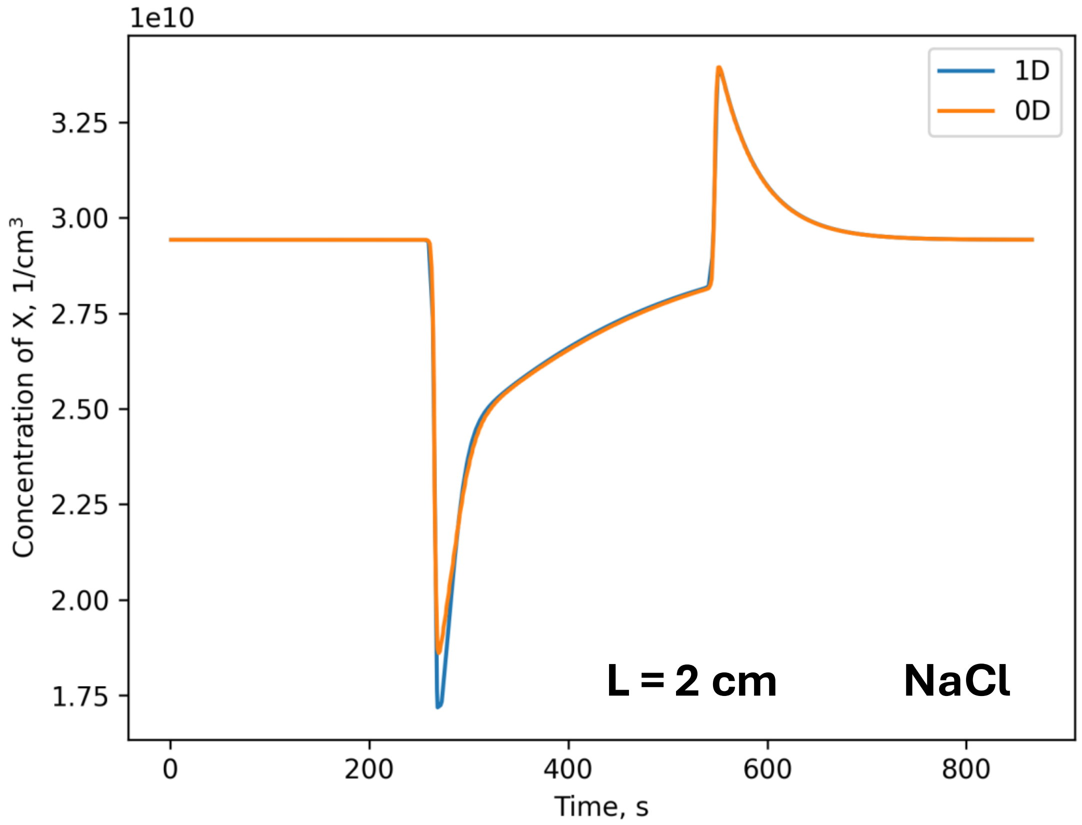
$$\gamma_{\mathrm{i}} \approx k_{\mathrm{ads}} S_{\mathrm{tot}} \sqrt{\frac{2\pi M}{R_{\mathrm{g}} T}}$$

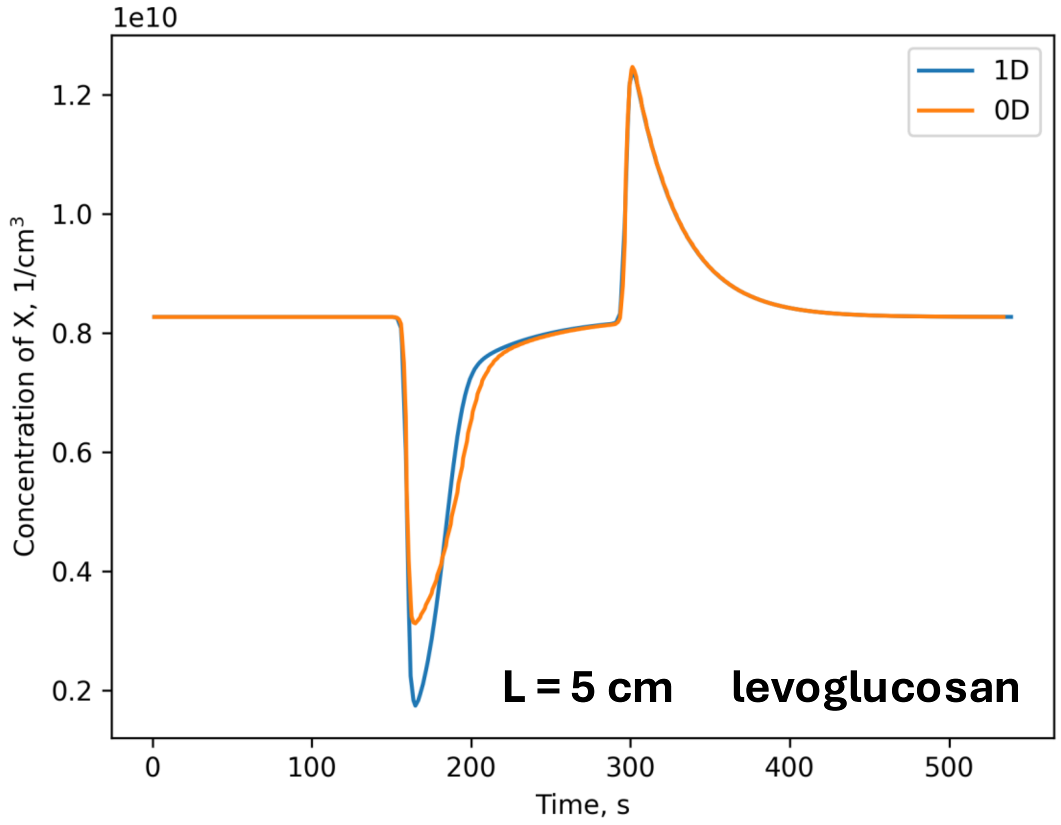
Initial uptake coefficient can be estimated from model parameters directly

$$\gamma = \frac{k_{\mathrm{ads}} X_{\mathrm{gs}} (S_{\mathrm{tot}} - X_{\mathrm{s}}) - \frac{R}{2} k_{\mathrm{des}} X_{\mathrm{s}}}{\omega}$$

$$\omega = X_{\mathrm{gs}} \sqrt{\frac{R_{\mathrm{g}} T}{2\pi M}}$$

Comparison of model performance





Conclusions and future work

Conclusions:

- With the developed framework, rate constant of the elementary reactions instead of effective kinetic parameters can be extracted from uptake experiments
- Fast fitting to experimental data
- Prediction of concentration-dependent uptake coefficients

Future work:

- Test the predictive power of the model
- Determine limitations of the CSTR model (when the 1D model needs to be used)

Acknowledgement

- Na Mao for experimental data
- Alex Lee for organizing files

Effective first order adsorption rate constant

At $t = 0$:

$k_{\text{eff}} = k_{\text{ads}} S_{\text{tot}}$

At steady state uptake, $\frac{dX_s}{dt} \approx 0$:

$k_{\text{eff}} = k_{\text{ads}}(S_{\text{tot}} - X_{\text{s,ss}})$

$X_{\text{s,ss}}$ can be estimated from the model or analytical expression:

$$K \equiv k_{\text{rxn}}(Y_{\text{tot}} - P)$$

$$E \equiv \frac{R}{2} k_{\text{des}} + K$$

$$T \equiv 4KS_{\text{tot}}k_{\text{ads}} + Rk_{\text{diff}}(2K + Rk_{\text{des}} + 2Xk_{\text{ads}})$$

$$X_{\text{s}} = \frac{T - \sqrt{T^2 - 32KRS_{\text{tot}}Xk_{\text{ads}}^2 k_{\text{diff}}}}{8k_{\text{ads}}K}$$