Dye Fading Kinetics Experiment

Obtain Kinetic Parameters from Dynamic Data

Introduction & Objectives

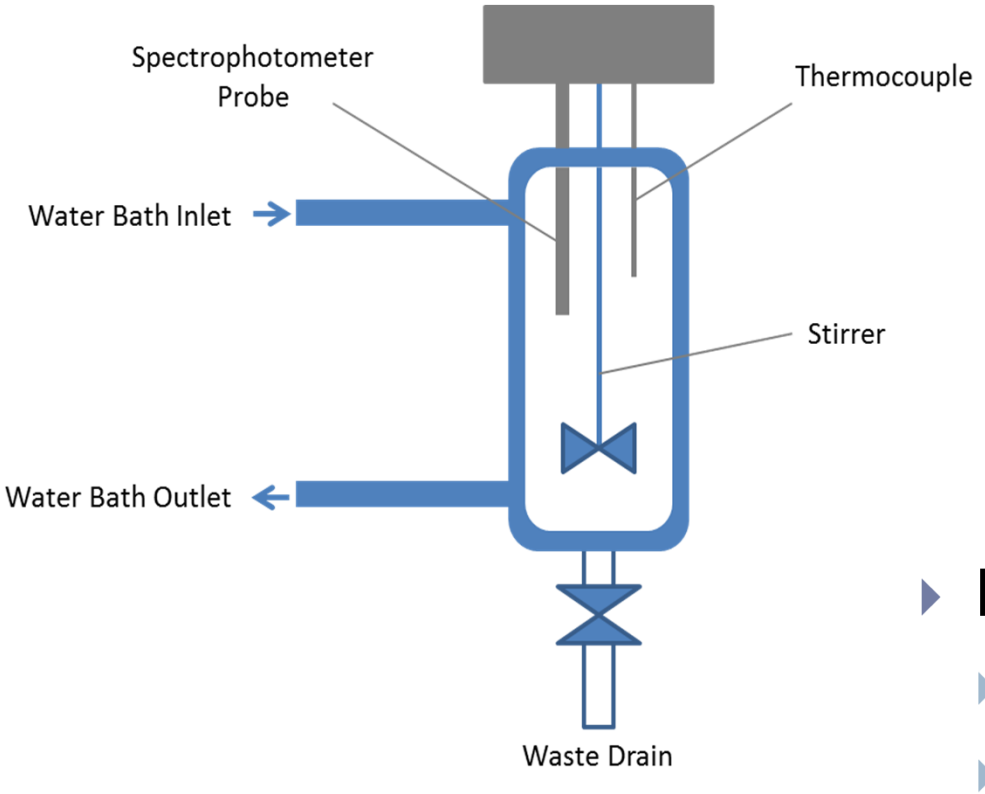
- Phenolphthalein desired to be used to find residence time of Industrial CSTR's

- Temperature Range: 60 – 120 °F
- Find:
  - Order
  - Arrhenius constants
  - Activation Energy
  - Heat of Reaction
  - Equilibrium constant

$$Ph + 2OH^- \rightarrow Ph^{2-} \qquad fast$$
$$Ph^{2-} + OH^- \leftrightarrow PhOH^{3-} \qquad slow$$

Experimental Methods

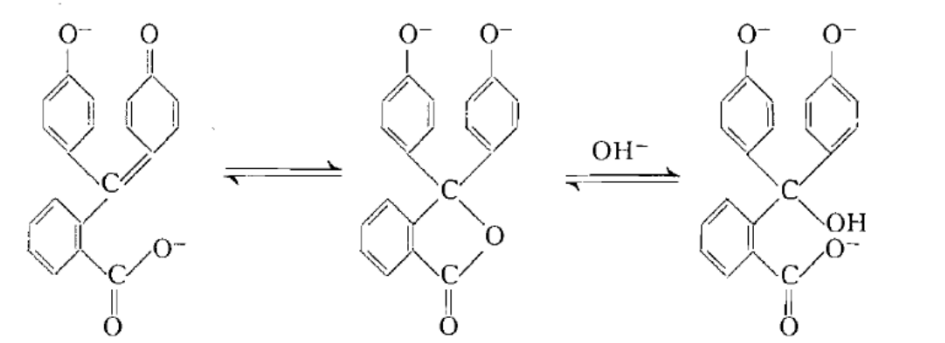
- Experimental Apparatus



- Experimental Design
  - Isothermal Runs
  - Dynamic Temperature Runs

Theory

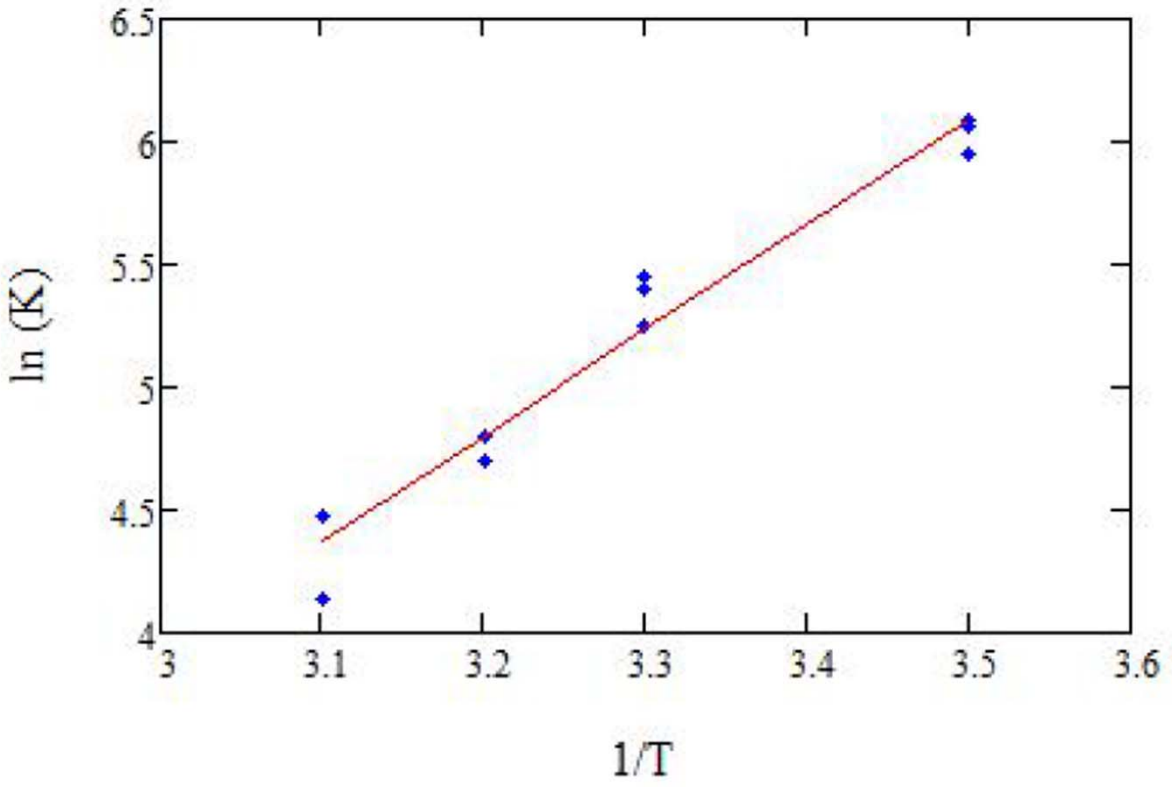
- Reaction
  - $Ph^{2-} + OH^{-} \leftrightarrow PhOH^{3-}$
- Elementary reactions rates
  - $-\frac{d[Ph^{-2}]}{dt} = -r = k_1[Ph^{-2}][OH^{-}] - k_2[PhOH^{-3}]$
  - Beer-Lambert's Law: relates the absorption of light to the properties of the material through which the light is travelling



Chen & Laidler, 1959

The Traditional Approach

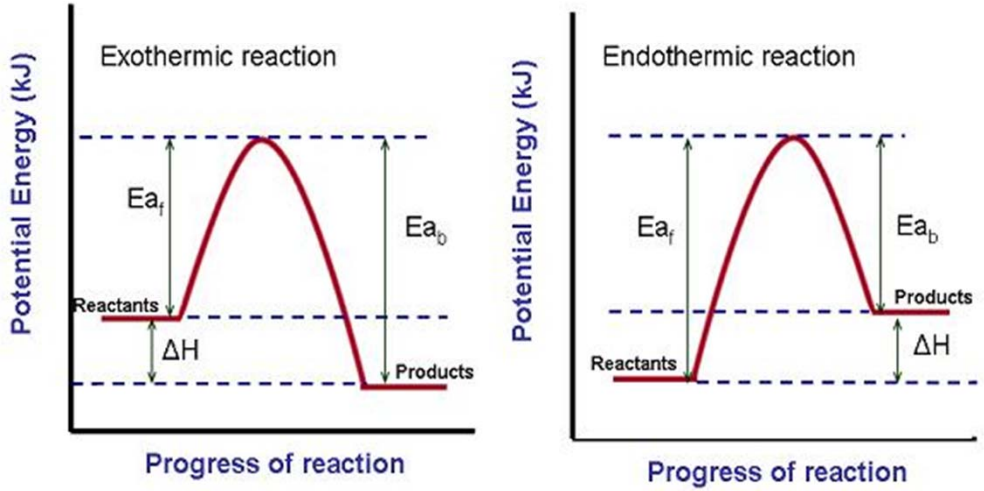
- Arrhenius Equation to find E_a and A
  - $k = \mathrm{A}\exp\frac{-E_a}{RT}$ or rearranged… $\ln(k) = \frac{-E_a}{R}\frac{1}{T} + \ln(A)$



Calculate the Heat of Reaction

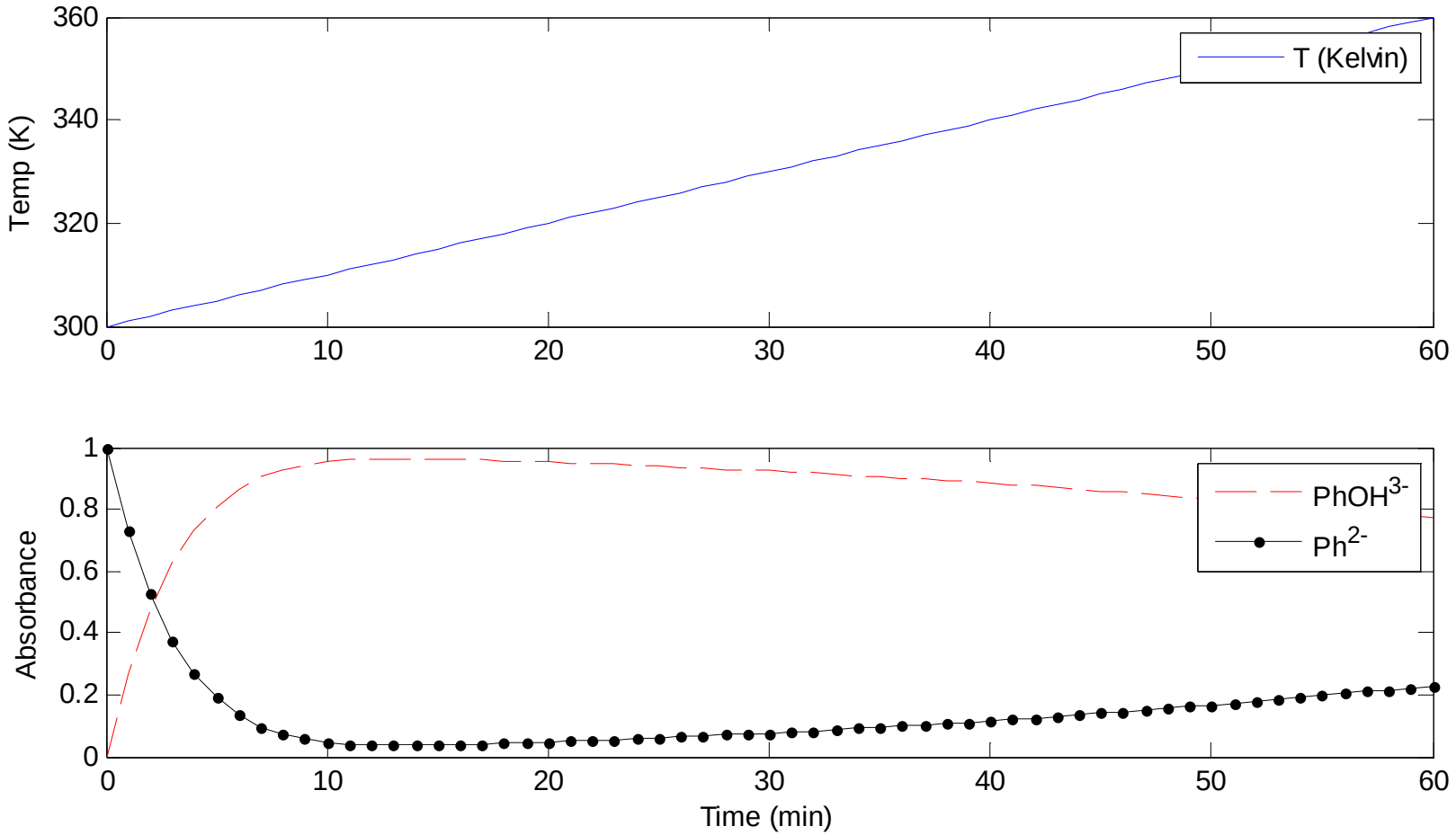
- Van't Hoff Equation to find $\Delta H°$
  - $ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

- $\Delta H°$ from E_a
  - $\Delta H^o = E_{a(fwd)} - E_{a(rev)}$
  - Exothermic: $-\Delta H^o$

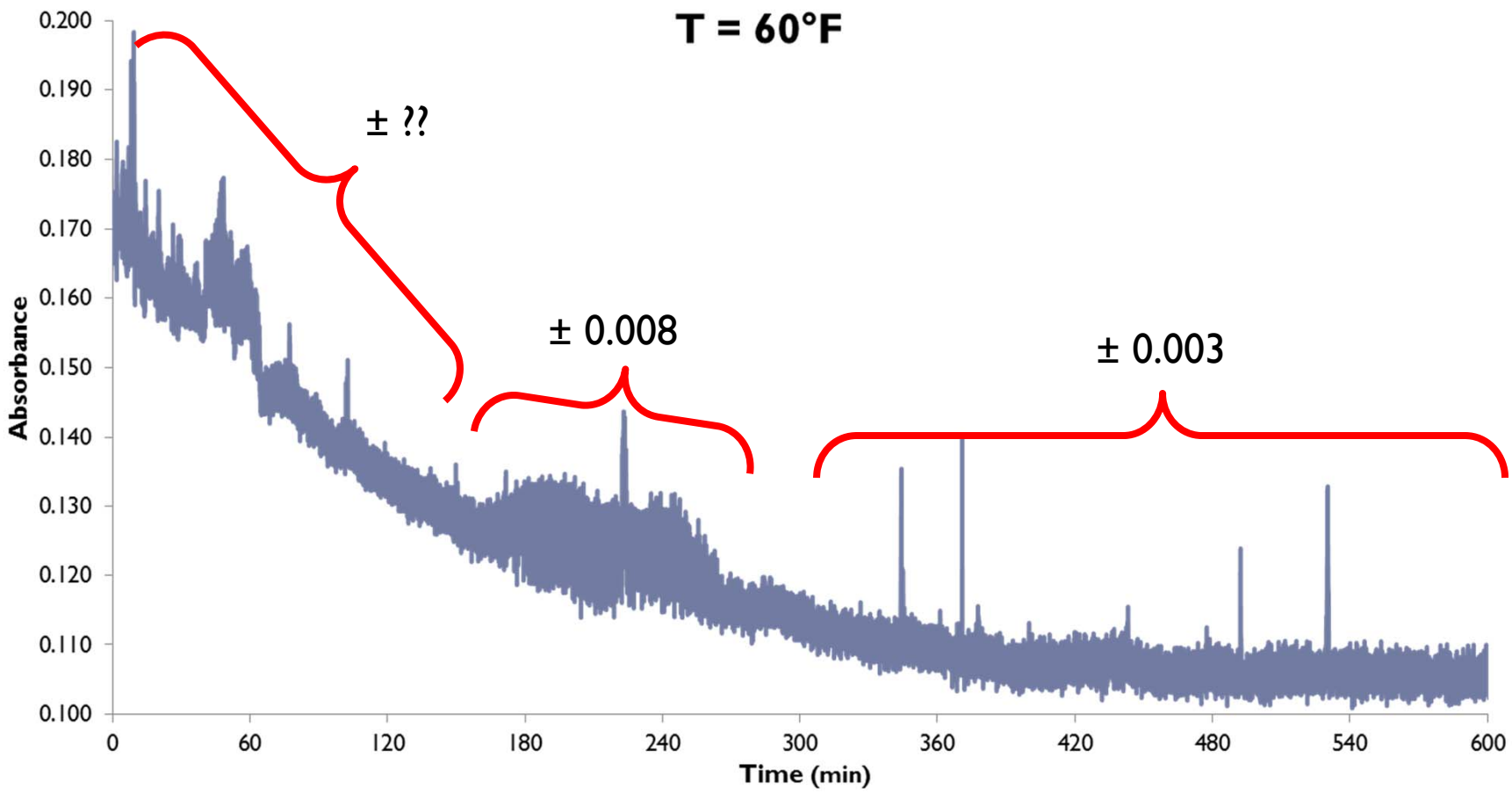


http://image.tutorvista.com/cms/images/44/Acitivation%20enthalpy.JPG

Simulate Dynamics

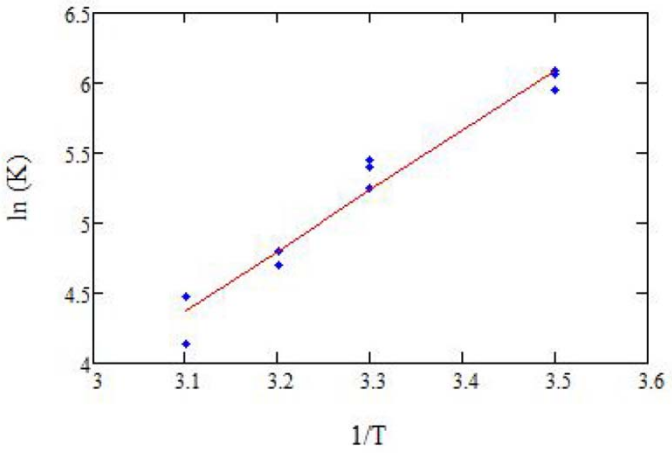


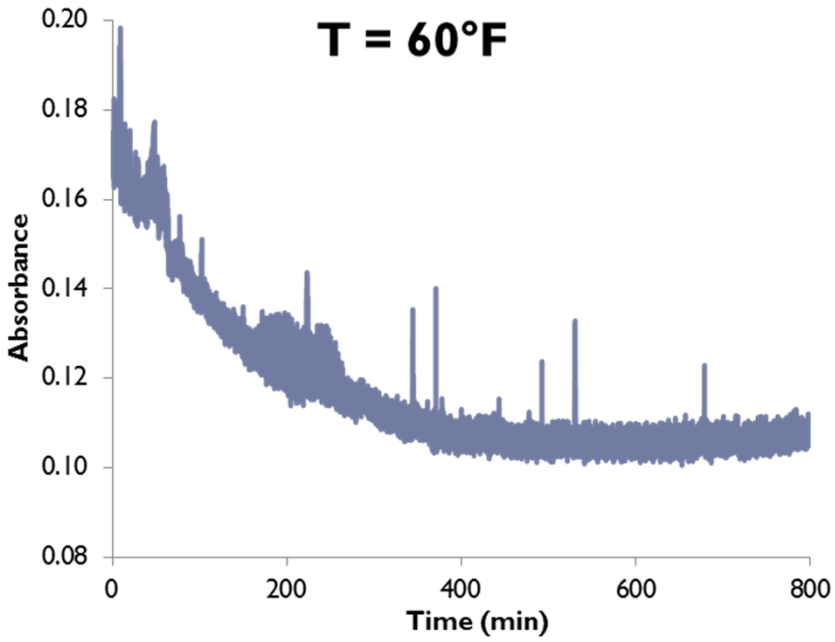
Noise

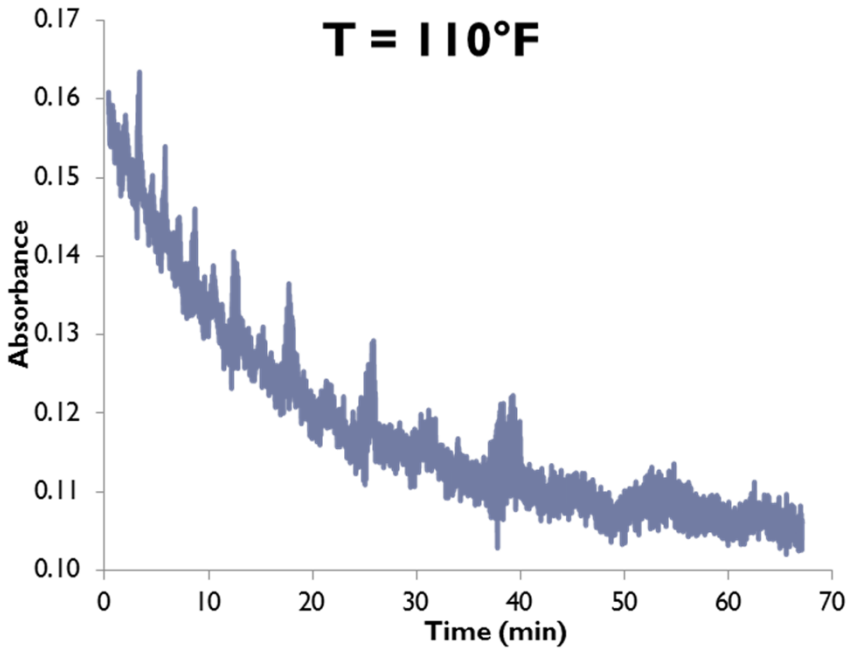

T = 60°F
± ??
± 0.008
± 0.003
Absorbance
0.200
0.190
0.180
0.170
0.160
0.150
0.140
0.130
0.120
0.110
0.100
0
60
120
180
240
300
360
420
480
540
600
Time (min)

Results – Data Summary

- Isothermal runs
  - Equilibrium

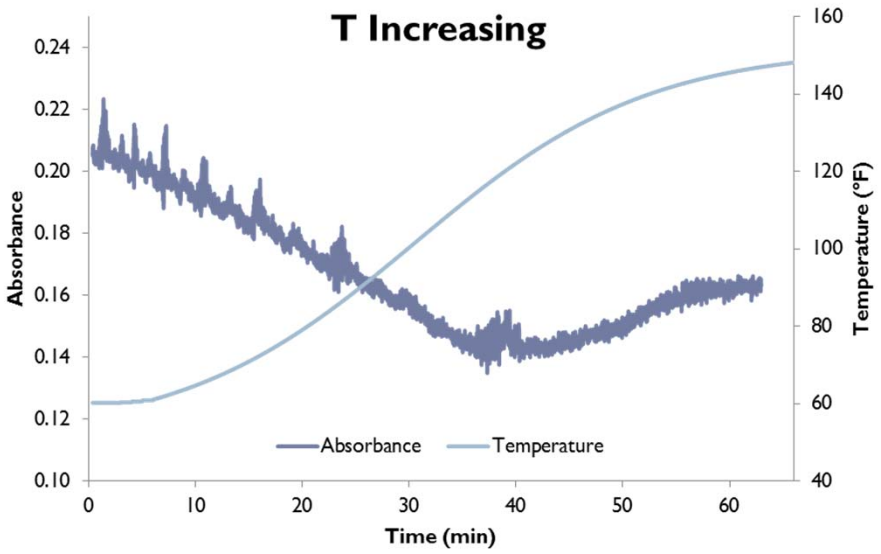


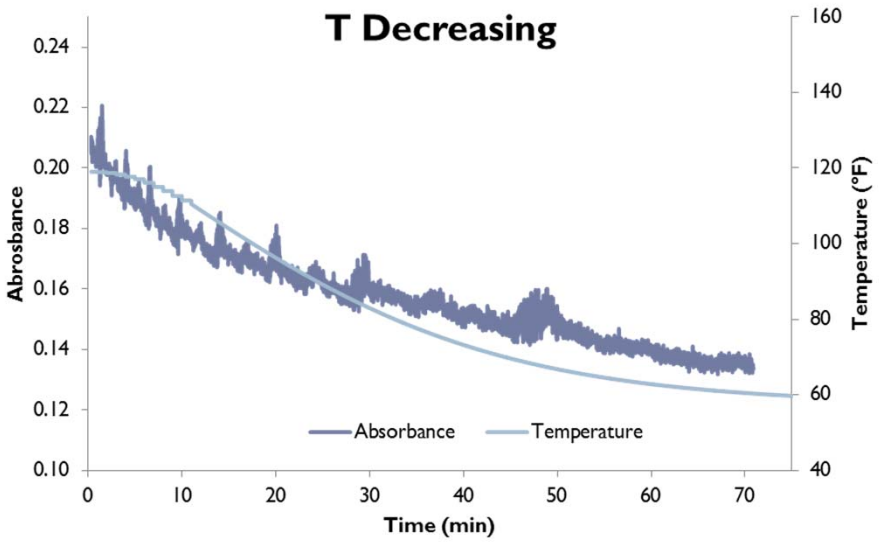




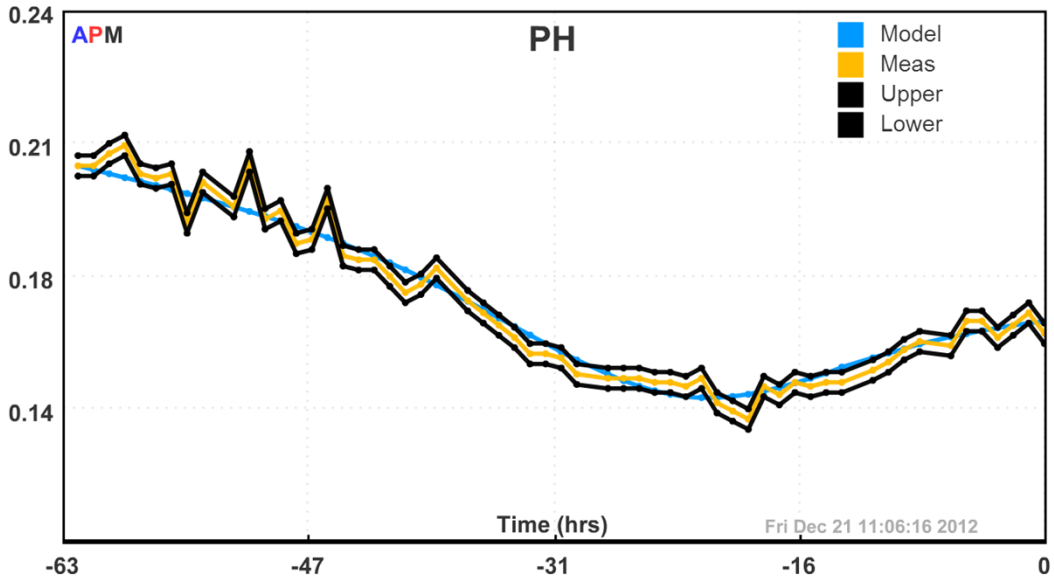
Non-isothermal Runs

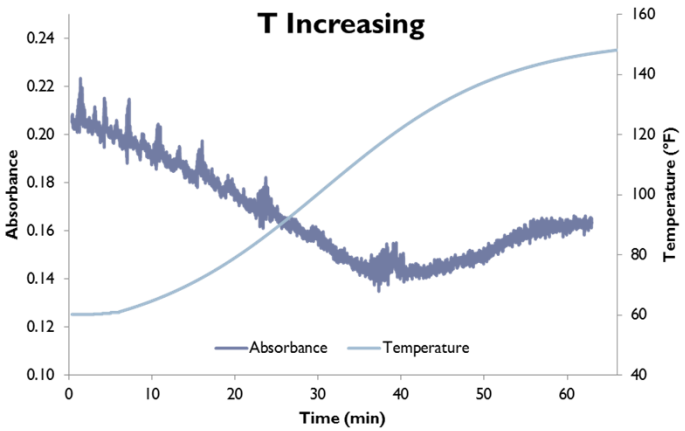
- No clear equilibrium





Estimate with Dynamic Data





- Solver required 34 Iterations
- Bounds on E_a and exponents
- Solution Time: <1.0 Second