In-Situ Methods for Kinetic Analysis

- Ideally, we would like to have a probe that can “ride along” with the molecules as the reaction proceeds, so that we have a virtually continuous account of the changing concentrations of species.
- What sort of probe can we use?

  Any method that gives an accurate measurement of some property of the system that is proportional to concentration or proportional to rate.

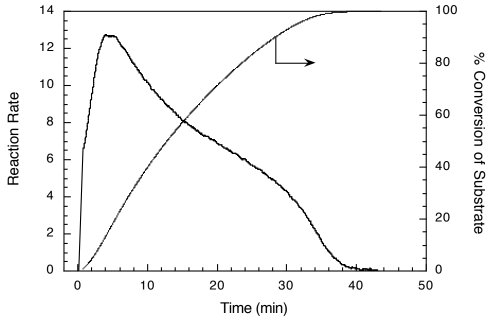
  - ***Differential (or derivative) methods*** measure a property that is proportional to the instantaneous reaction rate.
  - ***Integral methods*** measure a property that is proportional to concentration.

Experimental Kinetic Measurements

- Any method which measures ***differences*** in a property as a function of time will provide a more dramatic picture to the eye than one which measures ***accumulation*** (e.g. integral techniques).
- Features of the reaction profile are are more difficult to pick out by eye from a measure of **% conversion** vs. time compared to **rate** vs. time.
  - The induction period of rising rate lasts until ca. 10% conversion, but this appears only as a slight bend in the conversion plot.
  - The shoulder in rate at high conversion is also hard to spot in the conversion curve.

$$\text{rate of change of species } i = \frac{dC_i}{dt}$$

$$\text{\% conversion of species } i \;=\; 100 * \frac{1}{C_{i,0}} \int_{C_{i,0}}^{C_{i,t}} \left(\frac{dC_i}{dt} \right) dt$$



Integral Methods for Collecting Rate Data

- Sample collection and analysis:
  - sampling is conventionally used to obtain initial rate data
  - one rate datum point for every two samples taken!
- *In-situ* methods: spectroscopic
  - (FTIR, UV,Raman, etc)
  - usually measure concentrations by relying on Beer's Law.
  - to obtain reaction rate, we must take the derivative of concentration, dc/dt
- *In-situ* methods: Gas uptake measurements: P = f(t)
  - ideal gas law gives relationship between pressure and concentration
  - applicable to reactions where one of the reactants (or products) is gaseous (hydrogenations, oxidations, some polymerizations)

$$rate = \frac{\Delta C_i}{\Delta t} = \frac{C_i - C_{i-1}}{t_i - t_{i-1}}$$

$$A_i = \varepsilon b C_i$$

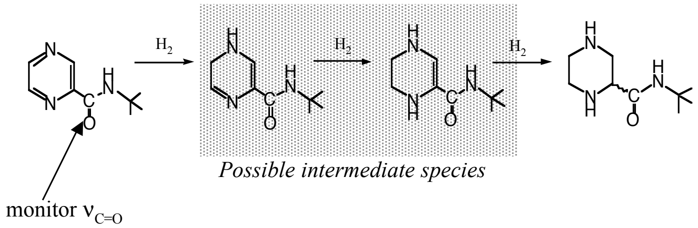
$$C_i = \frac{n_i}{V} = \frac{P}{RT}$$

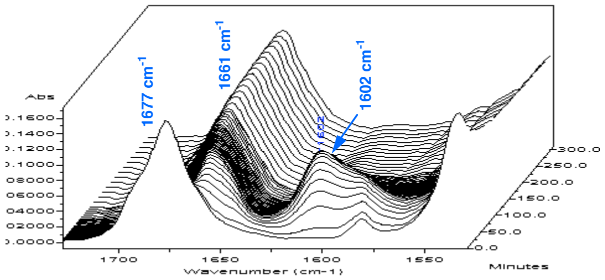
Differential Methods

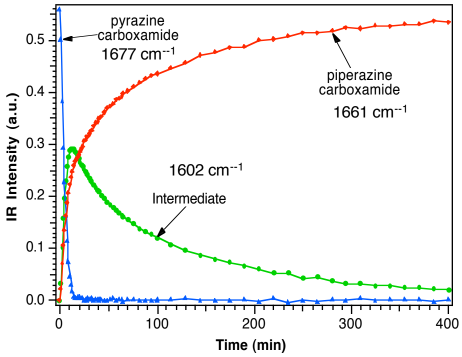
- *In-situ* methods: reaction calorimetry
  - measures reaction enthalpy, q, as a function of time
  - The heat consumed or evolved in a reaction is directly propotional to the reaction rate
  - Each datum point is a (rate, time) pair
  - Each datum point can be thought of as an "initial rate" measurement at a different substrate concentration.
  - Conversion may be obtained by integrating the heat flow curve.

$$q = \Delta H_{rxn} V \frac{dC_i}{dt} \qquad \%\ conversion = \frac{\int_0^t q(t)dt}{\int_0^{t_f} q(t)dt}$$

Example : *In-situ* FTIR Spectroscopy



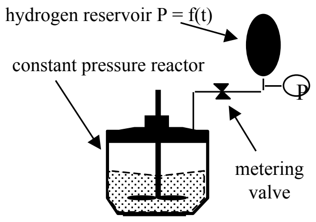


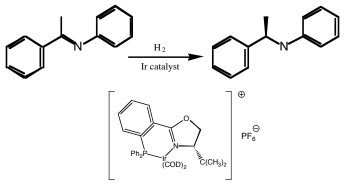


FTIR can give a concentration profile of reactants, intermediates, and products over the course of the reaction

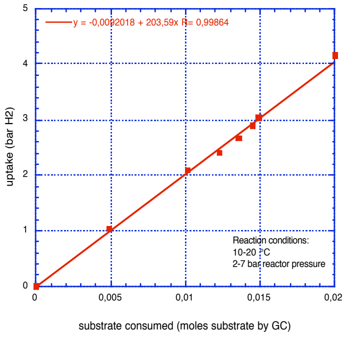
Sun, et al., *Thermochim. Acta*, **1996**, *289*, 189.

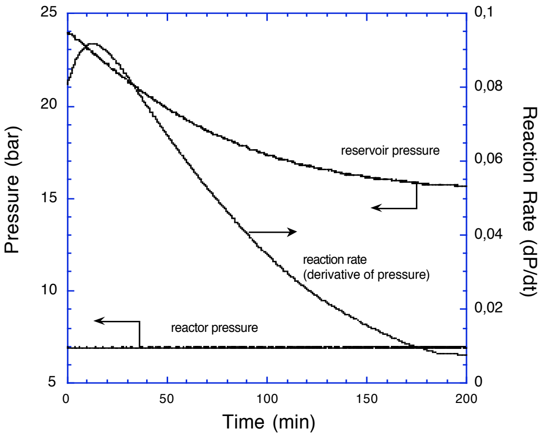
Example : Hydrogen Uptake Measurements





calibration curve between reservoir pressure and moles substrate consumed

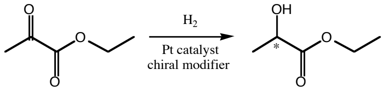


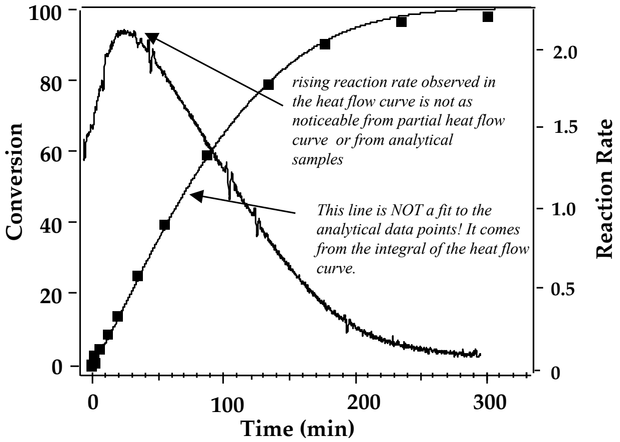


Rosner, Pfaltz, Blackmond

Example : Reaction Calorimetry

- Differential methods of measurement highlight rapid changes





rising reaction rate observed in the heat flow curve is not as noticeable from partial heat flow curve or from analytical samples

This line is NOT a fit to the analytical data points! It comes from the integral of the heat flow curve.

$$q = \Delta H_{rxn} \cdot V \cdot \frac{dC_i}{dt}$$

$$\%\ conversion = 100 \cdot \frac{\int_0^{t} q(t)dt}{\int_0^{t_f} q(t)dt}$$

heat flow calorimetry gives **kinetic** AND **thermodynamic** information about the reaction

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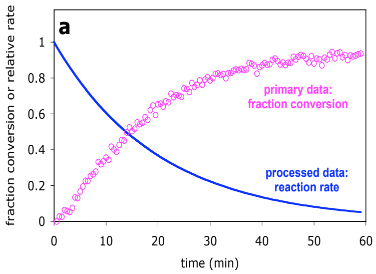
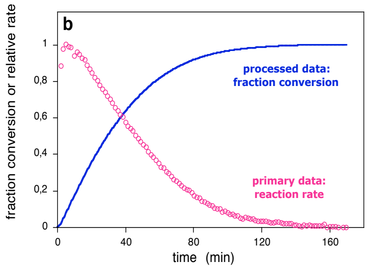
Developing a “Graphical Rate Equation”

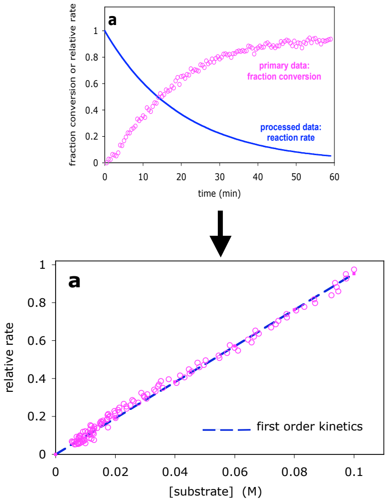
- We can turn our integral measurement into a differential curve (and vice versa) by differentiating it (or integrating it).
- The raw data are called the “primary data” and the derivative (or integral) curve is called the “processed” data.

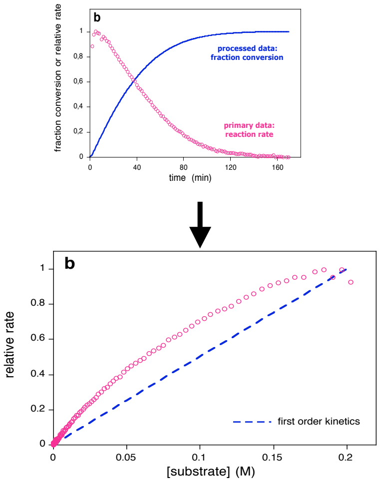




Developing a “Graphical Rate Equation”

- We make kinetic measurements as a function of time, but a reaction rate law gives rate as a function of concentration (or fraction conversion).
- If we combine our primary and processed data, we can develop a plot of rate vs. conversion (or concentration) -- a “graphical rate equation”.





Reaction Progress Kinetic Analysis

- Reaction progress kinetic analysis compared to classical kinetic methods:
  - we construct the entire rate vs. concentration curve from a single experiment rather than a series of initial rate experiments.
  - We make use of a visual approach (compare to integrating rate equations!) to assess the reaction’s “driving forces”.

- In this example, the plot of rate vs. concentration is linear, showing that the reaction obeys first order kinetics.

- In this example, the plot of rate vs. concentration shows curvature, suggesting that the rate law is more complex than a simple integer order.