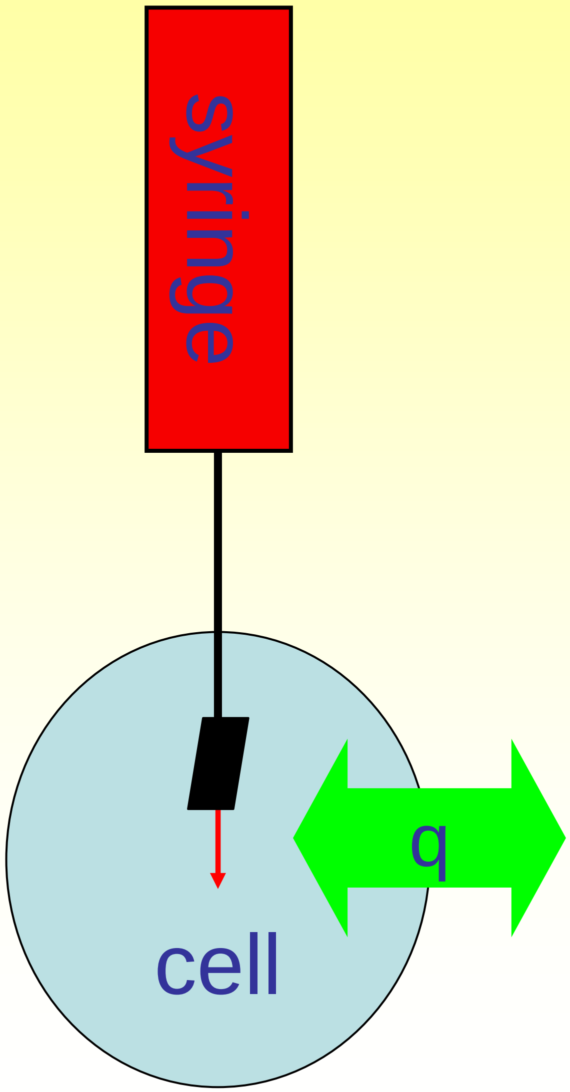
Techniques for Data Collection calorimetry

NJB

Calorimeters

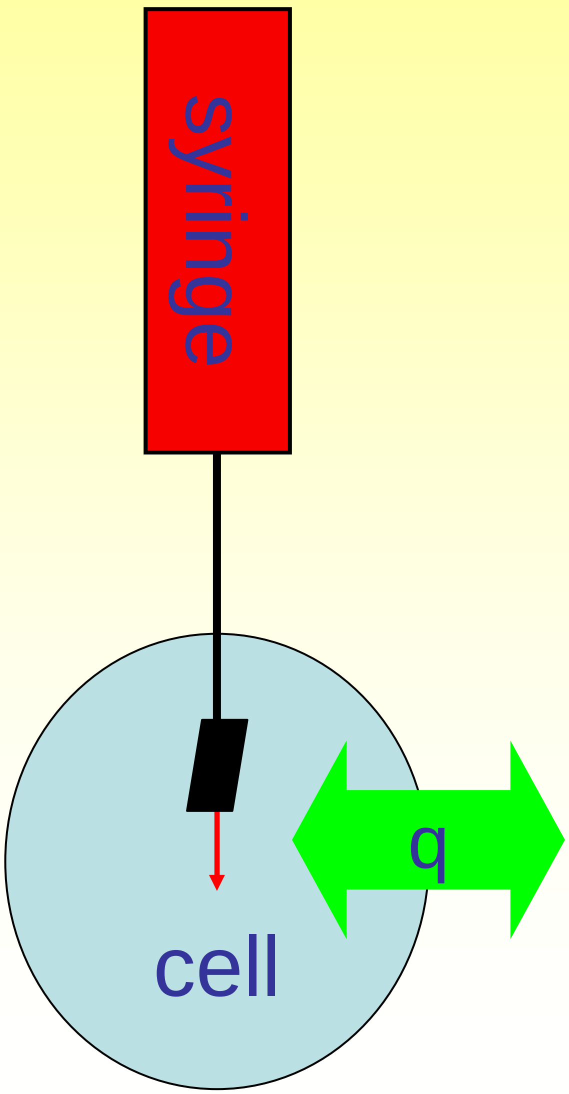
- Technique described using automated commercially available calorimeters but other setups feasible

Isothermal titration calorimetry



- Often used to study binding:
  - Guest in syringe is titrated into host in calorimeter cell
  - Heat effects of guest binding to host are measured and interpreted to give thermodynamic binding parameters

Kinetics by calorimetry



- Kinetics:
  - Reactant in syringe is titrated into solution containing other reactant or catalyst (enzyme) in calorimeter cell
  - Reaction heat effects are measured and interpreted in terms of rate equations

Kinetics by calorimetry

- Advantages
  - Measures rates
  - Label free (requires no chromophores or solution transparency)
  - High sensitivity: μcal s^{-1} (reaction heats typically kcal mol^{-1}, requires rates typically 1-10 nM s^{-1})
  - Automated data collection

Kinetics by calorimetry

- Disadvantages
  - High sensitivity (measures everything)
  - Requires matched solvents in syringe and cell
  - Cell is typically metal: less inert than glass
  - Cell is not fully closed (inert atmosphere difficult)

Kinetics by calorimetry

- Are you sure you know what your products are?
  (also true for, *e.g*., UV-visible)

heat flow linear with reaction rate

POC4SOC

$$power = \frac{dQ}{dt}$$

$$Q = n \cdot \Delta H_{\mathrm{app}} = [\mathrm{P}]_{\mathrm{total}} \cdot V_o \cdot \Delta H_{\mathrm{app}}$$

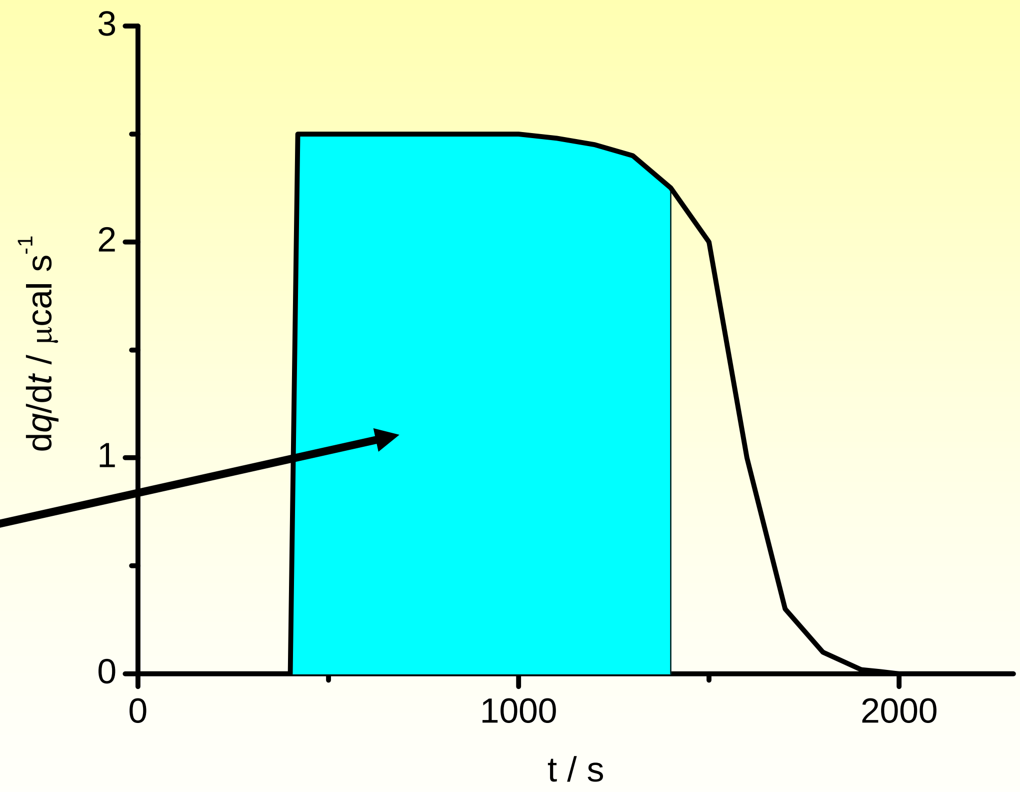
$$power = \frac{d[\mathrm{P}]_{\mathrm{total}}}{dt} \cdot V_o \cdot \Delta H_{\mathrm{app}}$$

$$\frac{d[\mathrm{P}]_{\mathrm{total}}}{dt} = \frac{1}{V_o \cdot \Delta H_{\mathrm{app}}} \cdot \frac{dQ}{dt}$$

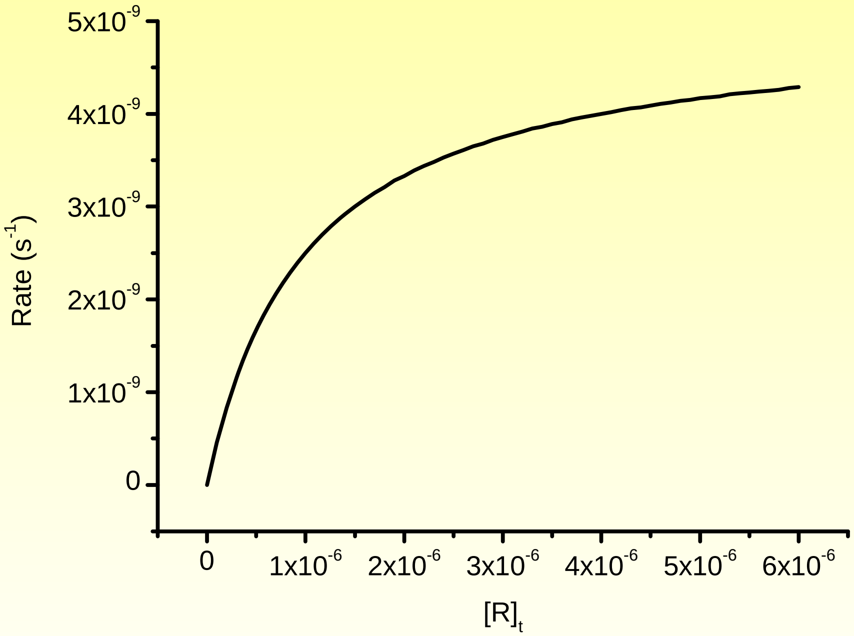
$$[\mathrm{R}]_t = [\mathrm{R}]_{t=0} - \frac{\int_0^t \frac{dQ}{dt}\,dt}{V_o \cdot \Delta H_{\mathrm{app}}} \cdot$$

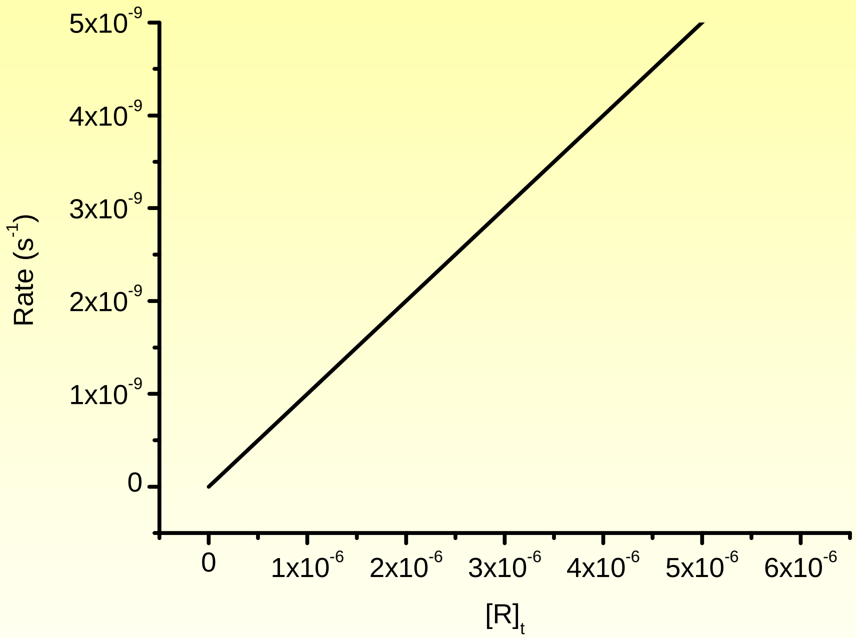
- remaining reactant concentration from extent of reaction

$$[\mathrm{R}]_t = [\mathrm{R}]_{t=0} - \frac{\int_0^t \frac{dQ}{dt}\,dt}{V_o \cdot \Delta H_{\mathrm{app}}}\cdot$$



Rate as function of [reactant]





Michaelis Menten

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}[\mathrm{C}]^{\mathrm{c}}$$