Developing a Kinetic Rate Expression from Batch Reactor Data

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Have the basic material balance (applies to all reactor types) given by:

$$\frac{dN_A}{dt} = F_{A0} - F_A + \int^{V} r_A dV$$

Batch reactor → no entry or exit flows (F_{A0}, $F_A = 0$)
Assume perfect mixing the batch reactor → the concentrations are the same everywhere (C_i and hence r_A is constant with respect to V)
As such, the mole balance reduces to:

$$\frac{dN_A}{dt} = r_A V$$

The batch reactor must have a constant volume (assume the fluid phase completely fills the reactor internal space) hence volume V is a constant with respect to time t. As such, can divide by sides by V to get:

$$\frac{dC_A}{dt} = r_A$$

We acknowledge that the rate expression must be some function of the fluid-phase concentrations:

$$\frac{dC_A}{dt} = r_A(C_i)$$

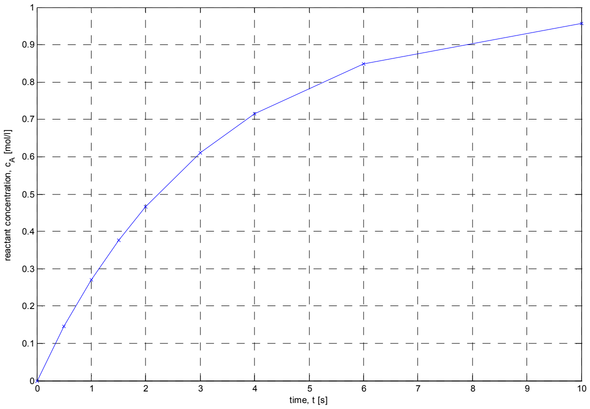
Simple kinetics, n^{th} order

We assume now that the rate depends only on the concentration of the reactant A but that the reaction order n is unknown. The batch reactor equation then becomes:

$$\frac{dC_A}{dt} = -kC_A^n$$

where k is the reaction rate constant [$mol^{1-n}.m^{-3(1-n)}.s^{-1}$]

We can charge the batch reactor with a certain amount of reactant A, and this will give us a certain initial concentration C_{A0}. As time goes on, the reactant is depleted due to the reaction, and hence a certain function $C_A(t)$ exists. A typical curve is shown below:



We recognize that, in addition to the reaction order, we also need to find the kinetic rate constant k. There are a number of methods we can use in finding these two parameters.

Method 1: Propose and test

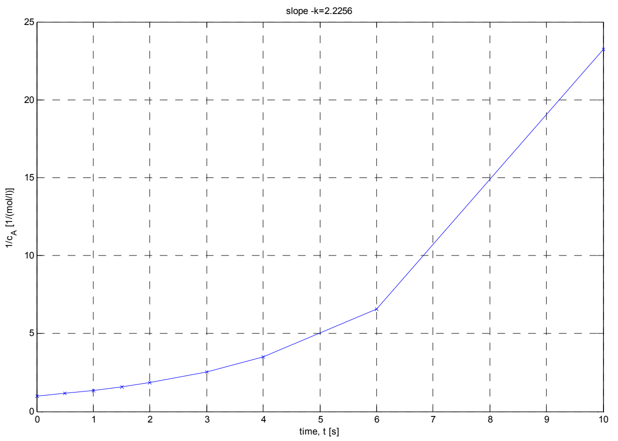
Propose a rate law and check whether the data matches this rate law. If it matches (and you must check if it does, at least by doing some statistical checks, at least through some superficial indices like the R_2 value), you can claim to have the solution.
Taking our example forward, let's assume the reaction was second order. The batch reactor equation then becomes:

$$\frac{dC_A}{dt} = -kC_A^2$$

which has the solution:

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + kt$$

Therefore a plot of $1/C_A$ -$1/C_{A0}$ vs t or $1/C_A$ vs t should give a straight line whose slope is k. Doing so, we get:



Two problems with this result: the line is clearly not straight, and it gives us a negative value for *k*. Second order is then a very poor choice.

Let try first order (*n* = 1) instead

$$\frac{dC_A}{dt} = -kC_A$$

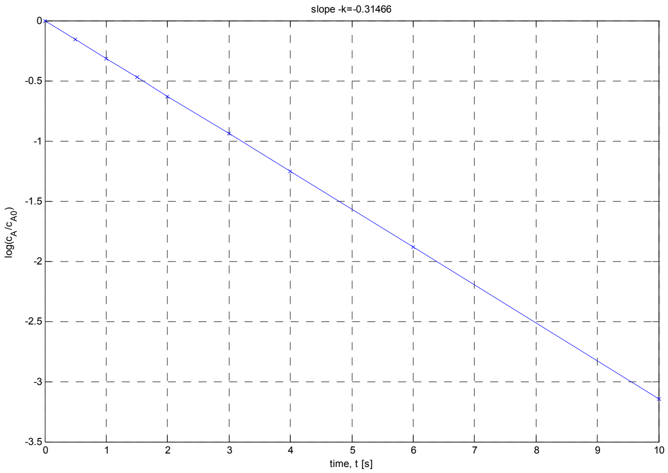
Which has the general solution

$$C_A = C_{A0}\exp(-kt)$$

We rearrange to get:

$$\ln\frac{C_A}{C_{A0}} = -kt$$

Which reveals that if we plotted $\ln(C_A/C_{A0})$ vs *t*. we should see a straight line and -*k* would be the slope of that line. Doing so, we get:



- a nice straight line with a positive value for *k*.

Method 2: Generalize the model

The method 1 used is a hit and miss affair – we must assume a value of *n*, and then see how the model looks for particular *n* values. A more rigorous approach would be to search among the values of *n* and *k* simultaneously for the best match.

If we generalize to an *n*-th order reaction, we get:

$$\frac{dC_A}{dt} = -kC_A^n$$

Sdd

$$C_A^{1-n}\Big|_{C_{A0}}^{C_A} = kt$$

Or $C_A^{1-n} - C_{A0}^{1-n} = kt$ or $C_A^{1-n} = C_{A0}^{1-n} + kt$

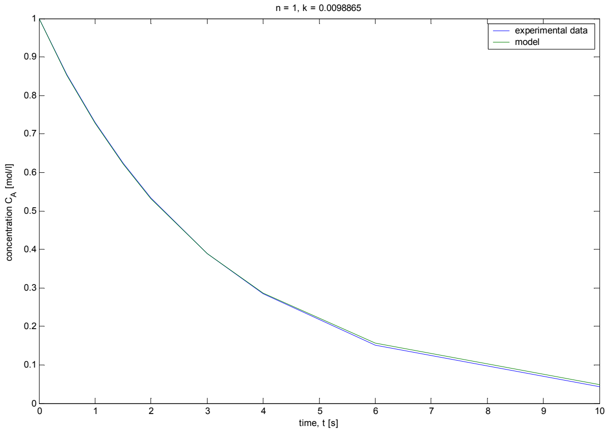
$$C_A = \exp\left(\frac{\ln(C_{A0}^{1-n} + kt)}{(1-n)}\right)$$

when n = 1, the model breaks down (since (1-n) in denominator) so we create the form:

$$C_A = \left(C_{A0}^{1-n} - kt\right)^{\frac{1}{1-n}} \text{ for n}\neq 1$$

$$C_A = C_{A0}\exp(-kt) \text{ for n=1}$$

We now write a solver which regresses to give:



The method is more general and more robust, but we find that the parameters it predicts are not very close to the exact values.

Importance of rxn kinetics – a bit of extra effort pays off to a large degree

- Craig Sheridan (constructed wetlands)
- Viran Pillay (hydrodynamics of bubble column reactors)