

Writing adsorption and reaction rate equations from mechanisms over solid surfaces

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In order to design a catalytic reactor, we need a rate equation that accurately predicts the rate of reaction as a function of fluid-phase concentrations over our solid catalyst. A rate equation derived from a "mechanism" - a list of elementary reaction steps - that provides a model of the molecular mechanism of the reaction is desired. Such a rate equation will be more reliable than an "empirical" rate equation that is simply a common function fit to experimental data. Here, we may say "gas" but the fluid could be a liquid or supercritical fluid.

We start with an assumed reaction mechanism and then write material balances and rate equations. The rate equations will be written under the following assumptions (Langmuir model):

- the surface is composed of identical, non-interacting sites with constant properties
- adsorbed components are distributed randomly over the surface and do not interact with neighboring adsorbed components except to participate in reaction steps (e.g., no change in adsorption energy with increasing coverage).

This model of adsorption over surfaces is simple and will only provide an approximate description. Since there are usually many other factors that complicate the situation over industrial heterogeneous catalysts, these approximate models will be useful in many cases.

Adsorption

Since you must have chemical components adsorb on a catalyst surface in order for reaction to happen, first consider the reversible adsorption of component A in which no change in A occurs.



Component A is a gas-phase component. S is a surface site. AS is a molecule of A adsorbed on the surface.

There are two things that I want you to do when deriving equations:

- 1) state the type of reactor and the conditions (transient, steady state) you are using
- 2) show the units of the terms in the equations

For (2) we write SI units because they are the simplest to use. One reason to do this is to increase your understanding of each term. Another is that a discrepancy in units can show when you forgot a term.

Here, choose a catalytic surface in a continuous flow stirred tank reactor or CSTR under isothermal, isobaric conditions. Then write the transient material balance equations.

Material balance for A

$$V (\text{m}^3) \frac{dC_A^g (\text{mol m}^{-3})}{dt (\text{s})} = r_{A, \text{flow in}} - r_{A, \text{flow out}} - r_{A, \text{ads}} + r_{A, \text{des}} (\text{mol s}^{-1}) \quad (2)$$

Material balance for AS

$$A(\text{m}^2) \frac{dC_{AS}^s (\text{mol m}^{-2})}{dt(\text{s})} = r_{A,ads} - r_{A,des} (\text{mol s}^{-1}) \quad (3)$$

Material balance for S

$$A \frac{dC_S^s}{dt} = -r_{A,ads} + r_{A,des} \quad (4)$$

In these notes C_i^g (mol/m^3) is the concentration of component i in the gas phase. Sometimes you may prefer to use partial pressures rather than concentration. For gases that can be well approximated by the ideal gas law,

$$C_i^g = \frac{n_i}{V} = \frac{p_i}{RT} \quad ; \quad p_i = \frac{n_i RT}{V} = C_i^g RT \quad (5)$$

C_i^s (mol/m^2) is the concentration of surface component i over the surface. Sometimes a surface concentration will be written S_i (mol/m^2).

Note that

$$\frac{dC_{AS}^s}{dt} = -\frac{dC_S^s}{dt} \quad (6)$$

This is true because there is a constant total number of surface sites. This is the "site balance" equation:

$$C_{total}^s = C_S^s + C_{AS}^s \quad (7)$$

Define the fractional surface coverage of surface component i

$$\theta_i = \frac{C_i^s}{C_{total}^s} \quad ; \quad 1 = \theta_S + \theta_{AS} \quad (8)$$

Often, θ_S will be written with a subscript "v" for vacant and the S will be left off the subscript "AS"

$$1 = \theta_v + \theta_A \quad ; \quad \theta_S = 1 - \theta_{AS} = 1 - \theta_A \quad (9)$$

Now write the rate equations

$$r_{A,flowin} - r_{A,flowout} (\text{mol s}^{-1}) = Q (\text{m}^3 \text{s}^{-1}) (C_{A,in}^g - C_A^g) (\text{mol m}^{-3}) \quad (10)$$

The rate of adsorption is proportional to the rate at which gas-phase molecules of A collide with empty (vacant) surface sites S. Under the assumptions of random distribution of adsorbed A over identical, non-interacting sites with constant properties, we can write the following:

$$r_{A,ads}(\text{mol s}^{-1}) = k'_{ads}(\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}) A(\text{m}^2) C_A^g(\text{mol m}^{-3}) C_S^s(\text{mol m}^{-2}) \quad (11)$$

$$= k'_{ads}(\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}) A(\text{m}^2) C_A^g(\text{mol m}^{-3}) C_{tot}^s(\text{mol m}^{-2})(1 - \theta_A) \quad (12)$$

$$r_{A,des}(\text{mol s}^{-1}) = k_{des}(\text{s}^{-1}) A(\text{m}^2) C_{AS}^s(\text{mol m}^{-2}) \quad (13)$$

$$= k_{des}(\text{s}^{-1}) A(\text{m}^2) C_{tot}^s(\text{mol m}^{-2}) \theta_A \quad (14)$$

Return to the material balance for AS

$$A C_{tot}^s \frac{d\theta_A}{dt} = r_{A,ads} - r_{A,des} \quad (15)$$

$$A C_{tot}^s \frac{d\theta_A}{dt} = k'_{ads} A C_A^g C_{tot}^s (1 - \theta_A) - k_{des} A C_{tot}^s \theta_A \quad (16)$$

$$\frac{d\theta_A}{dt} = k'_{ads} C_A^g (1 - \theta_A) - k_{des} \theta_A \quad (17)$$

Return to the material balance for gas-phase A

$$V \frac{dC_A^g}{dt} = r_{A,flow\ in} - r_{A,flow\ out} - r_{A,ads} + r_{A,des} \quad (18)$$

$$V \frac{dC_A^g}{dt} = Q(C_{A,in}^g - C_A^g) - k'_{ads} A C_A^g C_{tot}^s (1 - \theta_A) + k_{des} A C_{tot}^s \theta_A \quad (19)$$

For transient adsorption and desorption of A in the reactor from specified initial conditions, we can integrate the coupled differential equations from the surface and gas-phase material balances.

Steady-state adsorption

Here, consider steady-state operation. The time derivatives on the left hand sides are set to zero.

$$\frac{d\theta_A}{dt} = k'_{ads} C_A^g (1 - \theta_A) - k_{des} \theta_A \quad (20)$$

$$0 = k'_{ads} C_A^g (1 - \theta_A) - k_{des} \theta_A \quad (21)$$

$$\theta_A = \frac{K'_A C_A^g}{1 + K'_A C_A^g} \quad ; \quad K'_A (\text{m}^3 \text{mol}^{-1}) = \frac{k'_{ads}}{k_{des}} \quad (22)$$

$$V \frac{dC_A^g}{dt} = Q(C_{A,in}^g - C_A^g) - k'_{ads} A C_A^g C_{tot}^s (1 - \theta_A) + k_{des} A C_{tot}^s \theta_A \quad (23)$$

$$0 = Q(C_{A,in}^g - C_A^g) - k'_{ads} A C_A^g C_{tot}^s (1 - \theta_A) + k_{des} A C_{tot}^s \theta_A \quad (24)$$

$$0 = Q(C_{A,in}^g - C_A^g) / (A C_{tot}^s) - k'_{ads} C_A^g (1 - \theta_A) + k_{des} \theta_A \quad (25)$$

$$0 = Q(C_{A,in}^g - C_A^g) / (A C_{tot}^s) - 0 \quad (26)$$

$$C_A^g = C_{A,in}^g \quad (27)$$

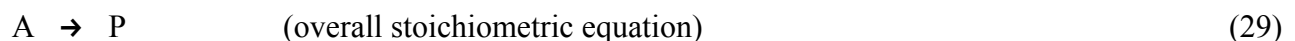
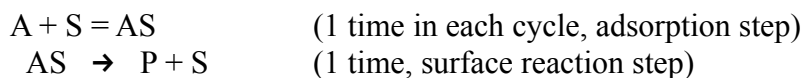
The most important equation above for this case of steady-state, equilibrium adsorption is called the "Langmuir isotherm"

$$\theta_A = \frac{K'_A C_A^g}{1 + K'_A C_A^g} \quad (28)$$

The plot of the surface coverage vs. C_A^g is linear at low C_A^g and then approaches an asymptote of one at large C_A^g .

Simple reaction

Consider this reaction mechanism:



We specify for this case that the rate of adsorption of product P is negligibly slow. This will be a good approximation when the reactor is operated such that the conversion to P is much less than the equilibrium conversion to P.

The material balance for gas-phase A in the CSTR stays the same as above. You should be able to write the material balance for gas-phase P. The balance for AS changes to add the reaction rate:

$$A (\text{m}^2) \frac{dC_{AS}^s (\text{mol m}^{-2})}{dt (\text{s})} = r_{A,ads} - r_{AS,des} - r_{A,rxn} (\text{mol s}^{-1}) \quad (30)$$

$$r_{rxn}(\text{mol s}^{-1}) = k_{rxn}(\text{s}^{-1})A(\text{m}^2)C_{AS}^s(\text{mol m}^{-2}) \quad (31)$$

$$= k_{rxn}(\text{s}^{-1})A(\text{m}^2)C_{tot}^s(\text{mol m}^{-2})\theta_A \quad (32)$$

Now consider steady-state operation.

$$0 = k'_{ads}AC_A^gC_{tot}^s(1-\theta_A) - k_{des}AC_{tot}^s\theta_A - k_{rxn}AC_{tot}^s\theta_A \quad (33)$$

$$0 = k'_{ads}C_A^g(1-\theta_A) - k_{des}\theta_A - k_{rxn}\theta_A \quad (34)$$

$$\theta_A = \frac{K''_A C_A^g}{1 + K''_A C_A^g} \quad (35)$$

$$K''_A(\text{m}^3 \text{mol}^{-1}) = \frac{k'_{ads}}{k_{des} + k_{rxn}} \quad (36)$$

$$r_{rxn}(\text{mol s}^{-1}) = k_{rxn}(\text{s}^{-1})A(\text{m}^2)C_{tot}^s(\text{mol m}^{-2})\theta_A \quad (37)$$

$$= \frac{k_{rxn}(\text{s}^{-1})A(\text{m}^2)C_{tot}^s(\text{mol m}^{-2})K''_A C_A^g}{1 + K''_A C_A^g} \quad (38)$$

Dividing both sides by the moles of surface sites $A(\text{m}^2)C_{tot}^s(\text{mol m}^{-2})$ we get

$$r_{rxn}(\text{s}^{-1}) = \frac{k_{rxn}(\text{s}^{-1})K''_A C_A^g}{1 + K''_A C_A^g} \quad (39)$$

This is the rate as a "turnover frequency" which is the moles of product formed per mole of surface sites per unit time.

The plot of the rate vs. C_A^g is linear at low C_A^g and then approaches a level rate asymptote at large C_A^g . Now go back to the gas equation.

$$V \frac{dC_A^g}{dt} = Q(C_{A,in}^g - C_A^g) - k'_{ads}AC_A^gC_{tot}^s(1-\theta_A) + k_{des}AC_{tot}^s\theta_A \quad (40)$$

$$Q(C_{A,in}^g - C_A^g) = \frac{k_{rxn}AC_{tot}^s K''_A C_A^g}{1 + K''_A C_A^g} \quad \text{at steady state.} \quad (41)$$

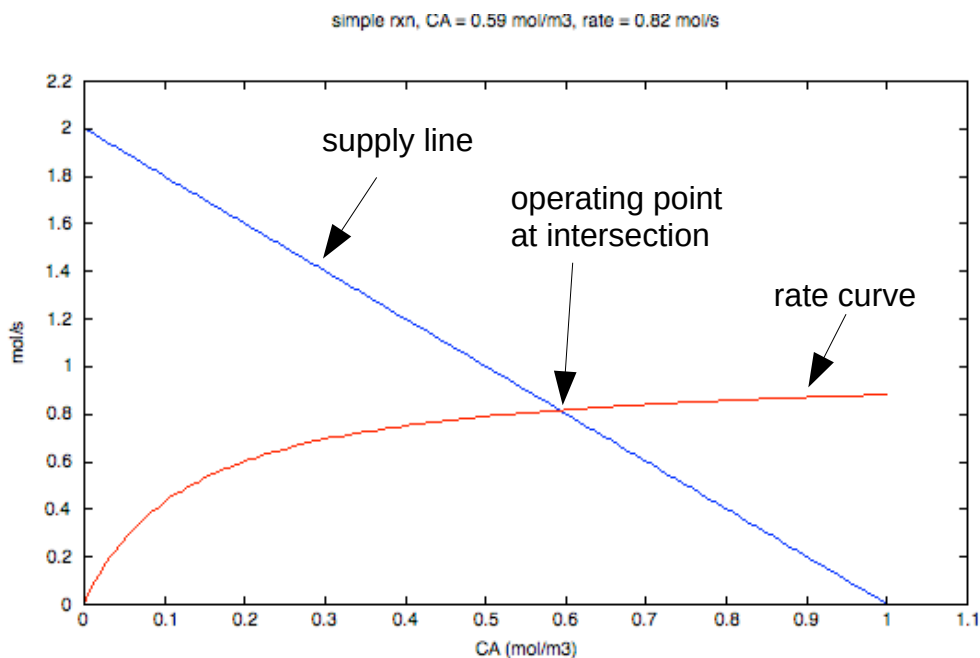
In words,

$$\text{"net rate of supply of A by flow"} = \text{"rate of consumption of A by reaction"} \quad (42)$$

$$\text{"supply line"} = \text{"rate curve"} \quad (43)$$

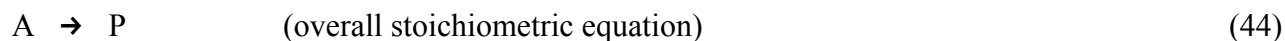
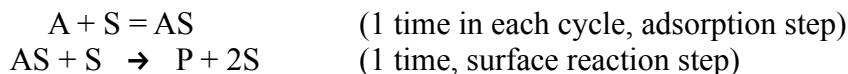
There is a geometric solution, as shown in the plot below. Plot the supply line and the rate curve vs. C_A^g . The intersection between the "supply line" and the "rate curve" is the steady-state solution.

There is also an algebraic solution for C_A^g .



Self inhibiting reaction

Consider this reaction mechanism:



We specify for this case that the rate of adsorption of product P is negligibly slow. This will be a good approximation when the reactor is operated such that the conversion to P is much less than the equilibrium conversion to P.

The surface reaction rate equation changes from the case above:

$$r_{rxn}(\text{mol s}^{-1}) = k'_{rxn}(\text{m}^2 \text{mol}^{-1} \text{s}^{-1}) A(\text{m}^2) C_{AS}^s(\text{mol m}^{-2}) C_S^s(\text{mol m}^{-2}) \quad (45)$$

$$= k'_{rxn}(\text{m}^2 \text{mol}^{-1} \text{s}^{-1}) A(\text{m}^2) C_{tot}^s(\text{mol m}^{-2})^2 \theta_A (1 - \theta_A) \quad (46)$$

Return to the material balance for AS

$$A C_{tot}^s \frac{d\theta_A}{dt} = r_{A,ads} - r_{A,des} - r_{A,rxn} \quad (47)$$

$$A C_{tot}^s \frac{d\theta_A}{dt} = k'_{ads} A C_A^g C_{tot}^s (1 - \theta_A) - k_{des} A C_{tot}^s \theta_A - k'_{rxn} A C_{tot}^s \theta_A (1 - \theta_A) \quad (48)$$

$$\frac{d\theta_A}{dt} = k'_{ads} C_A^g (1 - \theta_A) - k_{des} \theta_A - k'_{rxn} C_{tot}^s \theta_A (1 - \theta_A) \quad (49)$$

Return to the material balance for A

$$V \frac{dC_A^g}{dt} = r_{A,flow\ in} - r_{A,flow\ out} - r_{A,ads} + r_{A,des} \quad (50)$$

$$V \frac{dC_A^g}{dt} = Q(C_{A,in}^g - C_A^g) - k'_{ads} A C_A^g C_{tot}^s (1 - \theta_A) + k_{des} A C_{tot}^s \theta_A \quad (51)$$

Define the dimensionless gas concentration

$$\psi_i = \frac{C_i^g}{C_{A,max}^g} \quad (52)$$

$$\frac{d\psi_A}{dt} = \frac{Q}{V} (\psi_{A,in} - \psi_A) - \frac{A C_{tot}^s}{V C_{A,max}^g} (k'_{ads} C_{A,max}^g \psi_A (1 - \theta_A) - k_{des} \theta_A) \quad (53)$$

$$\frac{d\psi_A}{dt} = \kappa_{flow} (\psi_{A,in} - \psi_A) - \alpha (k_{ads} \psi_A (1 - \theta_A) - k_{des} \theta_A) \quad (54)$$

$$\kappa_{flow} (s^{-1}) = \frac{Q}{V} = \text{space velocity} \quad (55)$$

$$k_{ads} (s^{-1}) = k'_{ads} C_{A,max}^g \quad (56)$$

$$\alpha = \frac{A C_{tot}^s}{V C_{A,max}^g} \quad (57)$$

$$\alpha = \text{surface-to-gas capacity ratio} \quad (58)$$

Return to the material balance for P

$$V \frac{dC_P^g}{dt} = r_{P,flow\ in} - r_{P,flow\ out} - r_{P,ads} + r_{P,des} \quad (59)$$

$$V \frac{d C_P^g}{dt} = Q(C_{P,in}^g - C_P^g) + k'_{rxn} A C_{tot}^s \theta_A (1 - \theta_A) \quad (60)$$

$$\frac{d \psi_P}{dt} = \kappa_{flow} (\psi_{P,in} - \psi_P) + \alpha k'_{rxn} C_{tot}^s \theta_A (1 - \theta_A) \quad (61)$$

$$\frac{d \psi_P}{dt} = \kappa_{flow} (\psi_{P,in} - \psi_P) + \alpha k_{rxn} \theta_A (1 - \theta_A) \quad (62)$$

$$k_{rxn} (s^{-1}) = k'_{rxn} C_{tot}^s \quad (63)$$

With the dimensionless gas concentration, the surface equation becomes:

$$\frac{d \theta_A}{dt} = k_{ads} \psi_A (1 - \theta_A) - k_{des} \theta_A - k_{rxn} \theta_A (1 - \theta_A) \quad (64)$$

We could also define a dimensionless time by multiplying time t by κ_{flow} or one of the k (s^{-1}) values. Here we will not do that.

Steady-state operation

Now consider steady-state operation of the reactor. The time derivatives on the left-hand sides are set to zero. We won't bother to write the equation for P since, at steady state, we can get the concentration of P from the concentration of A and the overall stoichiometric equation.

$$0 = k_{ads} \psi_A (1 - \theta_A) - k_{des} \theta_A - k_{rxn} \theta_A (1 - \theta_A) \quad \text{surface A equation} \quad (65)$$

$$0 = \kappa_{flow} (\psi_{A,in} - \psi_A) - \alpha (k_{ads} \psi_A (1 - \theta_A) - k_{des} \theta_A) \quad \text{gas-phase A equation} \quad (66)$$

$$= \kappa_{flow} (\psi_{A,in} - \psi_A) - \alpha k_{rxn} \theta_A (1 - \theta_A) \quad (67)$$

Given specification of the input parameters

$$\kappa_{flow}, \psi_{A,in}, \alpha, k_{ads}, k_{des}, k_{rxn} \quad (68)$$

The surface and gas equations can be solved to find

$$\psi_A, \theta_A \quad (69)$$

The surface and gas equations can be written to show that they are both quadratic polynomials in θ_A . Thus, there is the possibility with this reaction of multiple solutions at steady state for some combinations of input parameters:

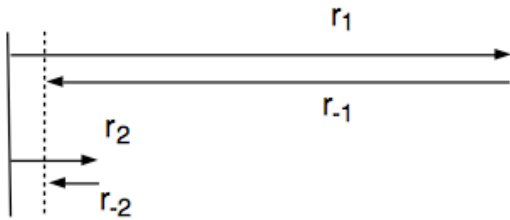
$$k_{rxn} \theta_A^2 - (k_{ads} \psi_A + k_{des} + k_{rxn}) \theta_A + k_{ads} \psi_A = 0 \quad \text{surface equation} \quad (70)$$

$$\theta_A^2 - \theta_A + \left(\frac{K_{flow}}{\alpha k_{rxn}} \right) (\psi_{A,in} - \psi_A) = 0 \quad \text{gas equation} \quad (71)$$

The quadratic equations somewhat deceptively imply that there are two solutions, however, they have to be solved simultaneously and there can be three solutions, as shown below.

Apply the Partial Equilibrium Approximation to step 1 and step 2 becomes the Rate Determining Step

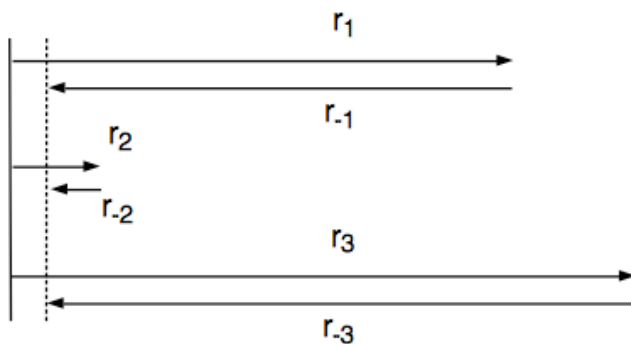
Consider a limiting case where the surface reaction rate in step 2 is slow with respect to the adsorption and desorption rates in step 1.



The arrows above are proportional to rates (mol/s). The difference between the forward and reverse rates for each step is the net rate of reaction. Be careful. This may imply to you that $K_{eq,1} \gg 1$, i.e., that equilibrium lies far to products on right, or high coverage of A in this surface reaction. It doesn't. The equilibrium constant for step 1, $K_{eq,1}$ can be $\ll 1$ and still have this sketch apply. The arrows in the sketch are rates, not the rate coefficients involved in $K_{eq,1}$.

Since the forward and reverse rates of step 1 are almost equal, we will apply the "Partial Equilibrium Approximation" (PEA) or "Quasi-Equilibrium Approximation" to step 1, and say that the step is in equilibrium in our math equations. This will allow us to express surface coverages in terms of fluid-phase concentrations and eliminate surface coverages from our equations to leave fluid concentrations.

We only have two steps in this reaction mechanism. When there are more steps, often one step will be slower than the others. In such cases, the PEA is applied to all steps except the slow, "rate determining step" (RDS) or "rate limiting step" (RLS). Below is a three-step mechanism with step 2 as the RDS. Any of the steps in a mechanism can be the RDS.



When developing a mechanism and rate expression that best fits our experimental data, we may propose that a step is rate determining and see how the resulting rate equation fits experimental data. Then try other steps as the RDS.

For our two-step mechanism, apply the PEA to step 1, and step 2 becomes the RDS

$$r_{ads} \approx r_{des} \quad \text{or} \quad r_1 \approx r_{-1} \quad (72)$$

$$k_{ads} \psi_A (1 - \theta_A) = k_{des} \theta_A \quad (73)$$

$$\theta_A = \frac{K_A \psi_A}{1 + K_A \psi_A} \quad \text{where} \quad K_A = \frac{k_{ads}}{k_{des}} \quad (74)$$

The surface A equation, Eqn 65, becomes

$$\alpha k_{rxn} \theta_A (1 - \theta_A) = \alpha \frac{k_{rxn} K_A \psi_A}{(1 + K_A \psi_A)^2} \quad (75)$$

The gas equation, Eqn 67, becomes

$$\kappa_{flow} (\psi_{A,in} - \psi_A) = \alpha \frac{k_{rxn} K_A \psi_A}{(1 + K_A \psi_A)^2} \quad [1/s] \quad (76)$$

The right hand side of Eqn 76 is the surface-to-gas capacity ratio α times the rate as a turnover frequency (mol product per mol sites per second). Rearranging to get units in (mol/s), we get

$$V C_{A,max}^g \kappa_{flow} (\psi_{A,in} - \psi_A) = A C_{tot}^s \frac{k_{rxn} K_A \psi_A}{(1 + K_A \psi_A)^2} \quad [\text{mol} / \text{s}] \quad (77)$$

In words,

"net supply of A to reactor by flow" = "rate of consumption of A by reaction"
 "supply line" = "rate curve"

The system equation is a cubic polynomial. From Eqn 76,

$$\psi_A^3 + a_2 \psi_A^2 + a_1 \psi_A + a_0 = 0 \quad (78)$$

$$a_2 = \left(\frac{2}{K_A} - \psi_{A,in} \right) ; \quad a_1 = \left(\frac{1}{K_A^2} + \frac{\alpha k_{rxn}}{K_A \kappa_{flow}} - \frac{2 \psi_{A,in}}{K_A} \right) ; \quad a_0 = - \left(\frac{\psi_{A,in}}{K_A^2} \right) \quad (79)$$

You can use the Matlab function "roots" to find the solutions. You can also use Wolfram Alpha on the web <www.WolframAlpha.com> to compute solutions. Solve

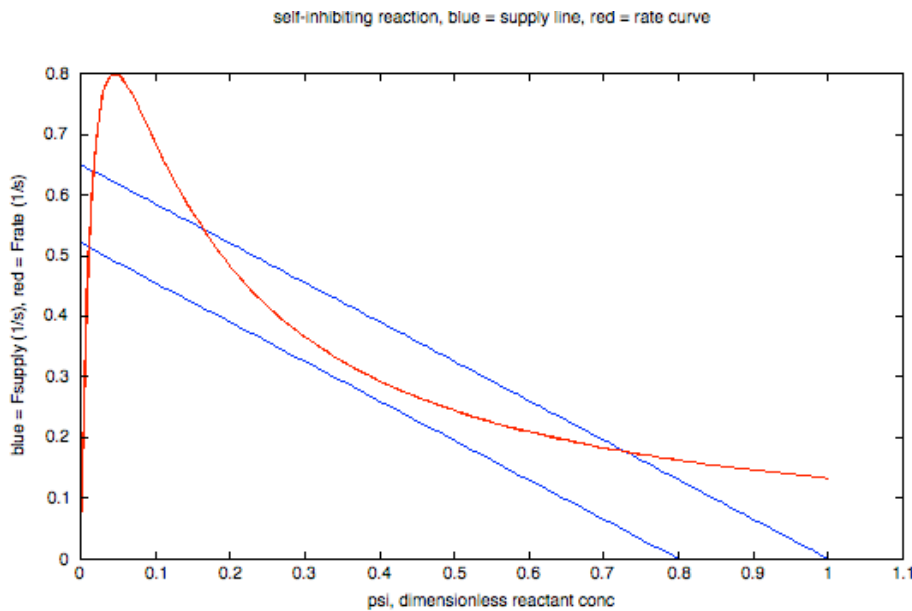
[x^3 + a2*x^2 + a1*x + a0 == 0, x]

The system equation also has a geometric construction and solution, as shown in the plot below.

Plot the "supply line" and the "rate curve" vs. ψ_A . The rate curve for this rate equation starts at the origin, increases linearly at low ψ_A and then curves and reaches a maximum, and then decreases to approach an asymptote of zero at large ψ_A .

In the plot shown here, Eqn 76 is plotted, such that the rate curve is the surface-to-gas capacity ratio α times the rate as a turnover frequency. The straight supply line has the negative slope of $-\kappa_{flow}$. The reactor "space velocity" is κ_{flow} . The line crosses the vertical axis at $(0, \kappa_{flow}\psi_{A,in})$ and crosses the horizontal axis at $(\psi_{A,in}, 0)$.

In the plot, the straight blue lines are the supply lines for two cases. The same maximum concentration was used in the definition of the dimensionless concentrations for the two cases shown. The red curve is the rate curve.



For relatively small or large values of $\psi_{A,in}$ you will only get one intersection of the supply line and rate curve. For intermediate values of $\psi_{A,in}$ you will get three intersections. Thus, with this self-inhibiting reaction, the reactor can exhibit multiple steady states: for the same set of rate constants, flow rate and inlet concentration, there can be two or more possible states of reactant concentration inside the reactor.

The middle solution of the three solutions (a) can't be reached by continuous variation of reaction parameters from some reasonable initial state, and (b) if it is obtained somehow, then it is an unstable steady state that will transition to one of the two stable steady states upon some infinitesimal disturbance to the system.

This can be explained graphically. For example, when ψ_A is increased slightly from the middle intersection (e.g., by dropping in some reactant), the net supply of A by flow at that new ψ_A becomes greater than the rate of consumption of A by reaction at that new ψ_A . Thus, the concentration in the reactor increases and the steady-state solution goes to the low-rate, high-concentration solution.

This reaction will exhibit a hysteresis loop in rate as the reactant feed concentration to the CSTR is varied.

Although it has a more complex mechanism, CO oxidation by O₂ over Pt can exhibit similar behavior in a CSTR. A colleague of mine at General Motors Research Labs observed hysteresis when changing CO concentrations. CO is a reactant that inhibits the reaction at high concentrations by inhibiting adsorption of O₂.

With application of the RDS, we now have a reaction "rate equation," which is

$$r_P(s^{-1}) = \frac{k_{rxn} K_A \psi_A}{(1 + K_A \psi_A)^2} \quad (80)$$

The rate in this form is called a "turnover frequency," which is the number of product molecules formed per site per unit time.

The denominator is squared because there are two sites involved in the rate determining step.

We can see that this is the turnover frequency by going back to the units in Eqn 46

$$r_{rxn}(\text{mol P formed } s^{-1}) = k'_{rxn}(\text{m}^2 \text{ mol}^{-1} \text{ s}^{-1}) A(\text{m}^2) C_{tot}^s(\text{mol m}^{-2})^2 \theta_A(1 - \theta_A) \quad (46)$$

$$\text{Divide both sides by the moles of surface sites: } \text{mol surface sites} = A(\text{m}^2) C_{tot}^s(\text{mol m}^{-2}) \quad (81)$$

$$r_{rxn} \left(\frac{\text{mol P formed}}{\text{mol surface sites} \cdot \text{s}} \right) = k'_{rxn}(\text{m}^2 \text{ mol}^{-1} \text{ s}^{-1}) C_{tot}^s(\text{mol m}^{-2}) \theta_A(1 - \theta_A) \quad (82)$$

$$r_{rxn} \left(\frac{\text{mol P formed}}{\text{mol surface sites} \cdot \text{s}} \right) = k_{rxn}(s^{-1}) \theta_A(1 - \theta_A) \quad (83)$$

where

$$k_{rxn}(s^{-1}) = k'_{rxn}(\text{m}^2 \text{ mol}^{-1} \text{ s}^{-1}) C_{tot}^s(\text{mol m}^{-2}) \quad (84)$$

Finally, we are back at our rate as turnover frequency

$$r_P(s^{-1}) = \frac{k_{rxn}(s^{-1}) K_A \psi_A}{(1 + K_A \psi_A)^2} \quad (80)$$