
Introduction to Chemical Engineering: Chemical Reaction Engineering

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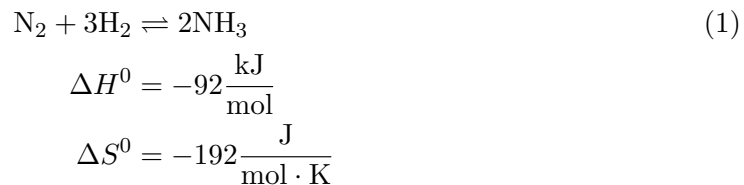
Introduction

Another important field of chemical engineering is that of chemical reaction engineering: considering the reactions that produce desired products and designing the necessary reactors accordingly. The design of reactors is impacted by many of the aspects you have encountered in the previous lectures, such as the equilibrium and the reaction rate, both dependent on temperature and pressure. While there is a great variety of types of reactors for different purposes, we will focus on three basic types: The batch reactor, the continuous stirred-tank reactor, and the plug-flow reactor.

1 Chemical reactions

1.1 Rate of reaction and dependence on temperature

We will once again look at the formation of ammonia (NH_3) from nitrogen and hydrogen (see section *Chemical equilibrium* of the thermodynamics chapter). This reaction follows the equation:



To find the Gibbs free energy of formation at room temperature, recall that

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0 & (2) \\ &= -92 \frac{\text{kJ}}{\text{mol}} + (298 \text{ K}) \left(0.192 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right) = -35 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Alternatively, one can also find the temperature for which $\Delta G = 0$, $T = \frac{\Delta H^0}{\Delta S^0} = 479 \text{ K} = 206^\circ\text{C}$. At this temperature the equilibrium favors neither the reactants nor the products. At lower temperatures ΔG is negative, so the products are favored and the reaction goes forward. At higher temperatures the equilibrium shifts to favor the reactants, as is expected for an exothermic reaction.

We also introduced the stoichiometric coefficient ν_i that describes how many molecules of species i react in each occurrence of the reaction. In general, a reaction between species A and B forming C can be written as



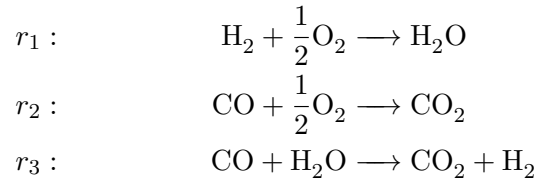
The rate of generation of each component i is then the product of the stoichiometric coefficient and the rate of the reaction, and relates to the rate of generation of every other component as follows:

$$r_i = \nu_i r \quad (4)$$

$$\frac{r_i}{\nu_i} = r = \frac{r_A}{\nu_A} = \frac{r_B}{\nu_B} = \frac{r_C}{\nu_C} \quad (5)$$

Remember that the stoichiometric coefficients for reactants are negative, while those of products are positive.

For systems of multiple chemical reactions the rates can be added to obtain the generation of component i for the whole network of reactions. As an example, take the oxidation of syngas, a mixture of carbon monoxide and hydrogen gas, where three reactions are to be considered, each having reaction rate r_j ($j = 1, 2, 3$):



Using the stoichiometric coefficients, the rate of generation or consumption of each component is then given by:

$$\begin{aligned} R_{\text{H}_2} &= -r_1 + r_3 \\ R_{\text{CO}} &= -r_2 - r_3 \\ R_{\text{H}_2\text{O}} &= r_1 - r_3 \\ R_{\text{CO}_2} &= r_2 + r_3 \\ R_{\text{O}_2} &= -\frac{1}{2}r_1 - \frac{1}{2}r_2 \end{aligned}$$

Note that in these equations the subscript in r_j indicates the reaction, whereas in Equations 4 and 5 it indicates the species. In general then, the rate of generation of component i in a system of reactions $j = 1 \dots N_r$ is the sum of the rates of generation across all reactions:

$$R_i = \sum_{j=1}^{N_r} r_{ij} = \sum_{j=1}^{N_r} \nu_{ij} r_j \quad i = A, B, \dots \quad (6)$$

The rate of each reaction then depends on the concentration of its reactants and the temperature, as described by the Arrhenius equation:

$$r = k(T) c_A^a c_B^b = k_0 e^{\frac{-E_A}{RT}} c_A^a c_B^b \quad (7)$$

where a and b are the reaction order with respect to reactant A and B, respectively. The overall order of the reaction is $n = a + b$.

1.2 Material balance

Consider a system of volume V with a stream entering and one exiting, as shown in Figure 1.

The accumulation of component i in this system is given by:

$$\underbrace{\frac{dn_i}{dt}}_{acc} = \underbrace{F_i^{in} - F_i^{out}}_{in-out} + \underbrace{G_i}_{net\ generation} \quad (8)$$

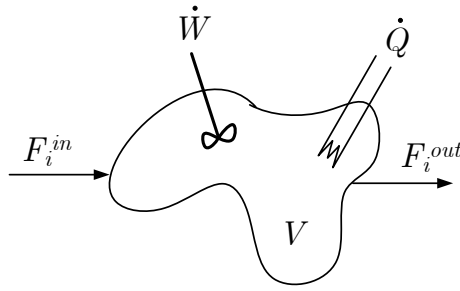


Figure 1: System of volume V with a stream entering and one exiting. F_i^{in} and F_i^{out} are the mole flows of component i into and out of the system, respectively. \dot{W} is the work done by the systems on its surroundings, and \dot{Q} is the heat flow into the system.

Here, the term G_i is the net generation for all reactions over the entire volume considered. Finding the net generation as well as the total amount of a component in the system requires integration over the whole volume:

$$\begin{aligned} n_i &= \int c_i dV \\ G_i &= \int R_i dV \end{aligned} \quad (9)$$

One assumption that is frequently made is that the system is homogeneous, at least over certain regions, so $n_i = Vc_i$ and $G_i = VR_i$. This also means that the composition of the exiting stream is equal to the composition in the entire volume. Further, the mole flow of a component is often written as the product of the volumetric flow and the concentration of the component in the stream, so $F_i = Qc_i$. If one further assumes that only one reaction is taking place, the material balance becomes

$$\frac{dn_i}{dt} = \frac{d(c_i V)}{dt} = Q^{in} c_i^{in} - Qc_i + r_i V \quad (10)$$

1.3 Conversion

The conversion of component i is the fraction of the reactant that undergoes reaction. It is denoted as X_i , where

$$X_i = \frac{\text{moles of component } i \text{ that reacted}}{\text{number of moles of component } i \text{ that were fed to the reactor}} \quad (11)$$

For a continuous reactor at steady state this is

$$X_i = \frac{Q^{in} c_i^{in} - Qc_i}{Q^{in} c_i^{in}} \quad (12)$$

The desired conversion is a key parameter in the design of reactors, as we will see.

1.4 Energy balance

Considering the volume in Figure 1, the energy balance can be written as:

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^{N_c} F_i^{in} e_i^{in} - \sum_{i=1}^{N_c} F_i^{out} e_i^{out} \quad (13)$$

The work in this equation consists of three terms: the so-called shaft work \dot{W}_s , and the volumetric work done by the entering stream on the system and by the system on the exiting stream.

$$\dot{W} = \dot{W}_s + P^{out}Q^{out} - P^{in}Q^{in} \quad (14)$$

The shaft work refers to the work done by the stirrer, for example, and is typically negligible in chemical systems, so $\dot{W}_s \approx 0$. The energy in the streams is summed for all N_c components, and can also be written in terms of concentrations and volume flow:

$$\sum_{i=1}^{N_c} F_i e_i = Q \sum_{i=1}^{N_c} c_i e_i = \frac{Q}{V} \sum_{i=1}^{N_c} n_i e_i = \frac{Q}{V} E \quad (15)$$

E is the sum of the internal energy U , the kinetic energy K , and the potential energy E_P . The kinetic and the potential energy are negligible in many chemical reaction engineering applications, so Equation 15 becomes

$$\frac{Q}{V} E = \frac{Q}{V} (U + K + E_P) \cong \frac{Q}{V} U \quad (16)$$

we know that U is a function of the enthalpy, pressure, and volume, so

$$\frac{Q}{V} U = \frac{Q}{V} (H - PV) = \frac{Q}{V} \sum_{i=1}^{N_c} n_i h_i - PQ = \sum_{i=1}^{N_c} F_i h_i - PQ \quad (17)$$

When this is applied for both streams, the term PQ cancels with the volumetric work from Equation 14, and the energy balance in Equation 13 becomes

$$\begin{aligned} \frac{dU}{dt} &= \dot{Q} - \left(\dot{W}_s + P^{out}Q^{out} - P^{in}Q^{in} \right) + \sum_i F_i^{in} h_i^{in} - \sum_i F_i^{out} h_i - P^{in}Q^{in} + P^{out}Q^{out} \\ \frac{dU}{dt} &= \dot{Q} + \sum_i F_i^{in} h_i^{in} - \sum_i F_i^{out} h_i \end{aligned} \quad (18)$$

If we are considering a homogeneous system where only one reaction takes place, $G_i = V\nu_i r$, and we can rewrite Equation 8 by solving for the flow out of the system:

$$F_i^{out} = F_i^{in} + V\nu_i r - \frac{dn_i}{dt} \quad (19)$$

Equation 18 then becomes

$$\frac{dU}{dt} = \dot{Q} + \sum_i F_i^{in} (h_i^{in} - h_i) - Vr \sum_i \nu_i h_i + \sum_i h_i \frac{dn_i}{dt} \quad (20)$$

Note that the sum of the enthalpies of each component multiplied by their corresponding stoichiometric coefficient is the heat of reaction, so $Vr \sum_i \nu_i h_i = Vr \Delta H_r$. At the same time, the difference in molar enthalpy between the entering stream and the reactor depends

on the temperatures and the specific heat of each component (assuming that there is no phase change):

$$h_i^{in} - h_i = h_i^{in}(T^{in}) - h_i(T) = \int_T^{T^{in}} c_{p,i} dT \cong c_{p,i}(T^{in} - T) \quad (21)$$

Further, the heat transfer into the reactor is $\dot{Q} = -UA(T - T_a)$, where U is the heat transfer coefficient, A is the heat transfer area, and T_a is the ambient temperature or the temperature of the heat transfer fluid. The left-hand-side of Equation 18 then becomes

$$\begin{aligned} \frac{dU}{dt} &= \frac{d(H - PV)}{dt} = \frac{d}{dt} \left(\sum_i n_i h_i - PV \right) \\ &= \sum_i n_i \frac{dh_i}{dt} + \sum_i h_i \frac{dn_i}{dt} - \frac{d(PV)}{dt} \\ &= \sum_i n_i c_{p,i} \frac{dT}{dt} + \sum_i h_i \frac{dn_i}{dt} - \frac{d(PV)}{dt} \\ &= V \sum_i c_i c_{p,i} \frac{dT}{dt} + \sum_i h_i \frac{dn_i}{dt} - \frac{d(PV)}{dt} \end{aligned} \quad (22)$$

Combining all this into equation 20, and canceling the term $\sum_i h_i \frac{dn_i}{dt}$ that shows up on both sides of the equation, we obtain

$$V \sum_i c_i c_{p,i} \frac{dT}{dt} - \frac{d(PV)}{dt} = -UA(T - T_a) + Q^{in} \left(\sum_i c_{p,i} c_i^{in} \right) (T^{in} - T) + Vr(-\Delta H_r) \quad (23)$$

2 Three types of reactors

2.1 Batch

A batch reactor is a discontinuous reactor. It is essentially a stirred tank that is filled with the reactants before the reaction starts and emptied after it has run to completion (or to the extent that is needed). An example of this would be the baking of a cake. All the ingredients are placed in the mold, and then the temperature is increased in the oven to the necessary reaction temperature. When the reactions that make up the baking process have run their course to the desired extent, they are stopped. One of the disadvantages of this type of reactor is that for large production quantities the reaction has to be done multiple times in series. This requires the emptying and refilling of the reactor, often accompanied by cooling it off first and heating it up with the new batch. This large number of steps takes time and attention, and thereby reduces the productivity of the reactor. On the other hand, these reactors have the advantage that if multiple similar but different reactions are needed, often the same equipment can be used, and the additional effort is comparatively small. A schematic of a batch reactor can be seen in Figure 2.

2.2 Continuous stirred tank reactor (CSTR)

A continuous stirred tank reactor is like a batch reactor in that it consists of a tank and a stirrer, however with the addition of an inlet and an outlet that allow for a constant flow

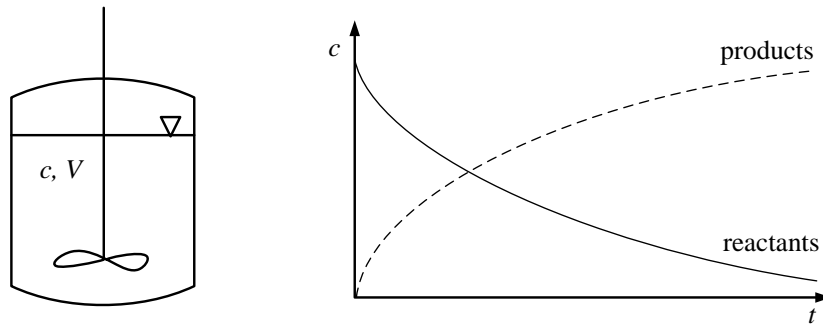


Figure 2: Schematic of a batch reactor and typical evolution of the concentration of reactants and products in a batch reactor

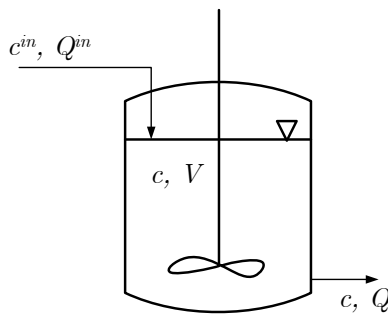


Figure 3: Schematic of a continuous stirred tank reactor (CSTR)

into and out of the reactor. Once the reactor is started up and reaches steady-state, it is usually assumed to have a constant volume as well as constant and homogeneous temperature, pressure, and composition. While continuous processes don't have the variability of batch processes, and during start-up will produce product that does not meet specifications, they have a number of advantages that make them attractive to use. For one, continuous reactors don't have to be cooled off, emptied, cleaned, refilled, and then heated to operating temperature. For another, if a reaction produces heat and the reactor needs to be cooled, the cooling duty for a CSTR is constant, and can be tuned as needed. For a batch reactor the cooling duty needed would vary with the reaction rate, and insufficient cooling can lead to a runaway reaction. Additionally, the product from one reactor is often used in subsequent steps for other reactions. If multiple steps are done in series in batch reactors, and each step takes a different amount of time, the intermediate products need to be stored in buffer tanks. These tanks can be eliminated or greatly reduced in size if each reactor produces a steady stream that can be fed to the next reactor. If a process has to be done in batches, several reactors are often used in parallel, shifted in time to give a continuous stream from the group of reactors. See Figure 3 for a schematic representation of a CSTR.

2.3 Plug flow reactor(PFR)

Another type of continuous reactors is the plug flow reactor, or PFR. It is a tubular reactor, meaning that it consists of a long cylindrical pipe through which the reaction mixture is

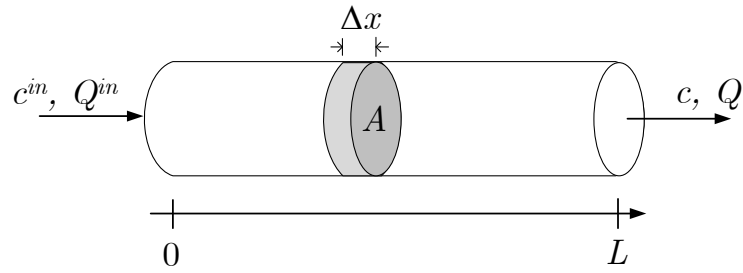


Figure 4: Schematic of a plug-flow reactor (PFR)

flowing steadily. Typically the assumption is made that the temperature, pressure, and composition do not vary radially within the pipe, creating a “plug” that flows through the reactor. As the reactants flow through the PFR, they are consumed, creating a concentration profile along the length of the pipe. While these reactors can have a heating or cooling duty requirement that varies along the reactor, the reactor volume necessary to reach a particular conversion is lower than for a CSTR, while keeping the advantages of a continuous process.

3 Material balances in chemical reactors

3.1 Batch

A batch reactor has no flow into or out of the reactor:

$$Q^{in} = Q = 0 \quad (24)$$

This reduces the general mole balance from equation 10 to

$$\begin{aligned} \frac{d(c_i V)}{dt} &= r_i V \\ V \frac{dc_i}{dt} + c_i \frac{dV}{dt} &= r_i V \end{aligned} \quad (25)$$

Often, the reactor volume in a batch process is nearly constant. In this case, the equation reduces even further, and the rate of change in concentration is simply the rate of reaction. If this is not the case, one can still rewrite equation 25. Both cases can be seen here:

$$\begin{aligned} \frac{dV}{dt} = 0 & \qquad \qquad \qquad \frac{dc_i}{dt} = r_i \\ \frac{dV}{dt} \neq 0 & \qquad \qquad \frac{dc_i}{dt} + c_i \frac{d \ln V}{dt} = r_i \end{aligned} \quad (26)$$

Calculating the conversion X_i for a batch process is relatively straightforward. It is the difference between the number of moles of reactant i initially in the reactor and those left at the end of the reaction divided by the total number at the beginning. It can then be related to the reactor volume and the reaction rate:

$$X_i = \frac{n_i^0 - n_i}{n_i^0} \quad (27)$$

$$dN_i = -N_i^0 dX \quad (28)$$

$$\frac{dX_i}{dt} = \frac{-r_i V}{n_i^0} \quad (29)$$

$$\frac{dX_i}{dt} = \frac{-r_i}{c_i^0} \quad (30)$$

where c_i^0 is the initial concentration of reactant i .

3.2 Continuous stirred tank reactor (CSTR)

A CSTR, as mentioned earlier, has a feed stream entering the reactor and a product stream exiting. It is usually assumed to be well-mixed, giving it a constant temperature, composition, and reaction rate throughout its entire volume. It is almost always operated at steady state, meaning that after start-up is complete, the pressure, temperature, composition, and reaction rate no longer vary in time. Once steady-state is reached, the number of moles of any given species no longer changes, and the flow out of the reactor matches the feed flow.

$$\frac{dn_i}{dt} = 0 \quad \text{and} \quad Q^{in} = Q \quad (31)$$

This allows us to simplify the mole balance from equation 10 as follows:

$$\begin{aligned}\frac{dn_i}{dt} &= Q^{in} c_i^{in} - Q c_i + r_i V \\ 0 &= Q c_i^{in} - Q c_i + r_i V \\ c_i - c_i^{in} &= r_i \frac{V}{Q} = r_i \tau\end{aligned}\tag{32}$$

Here we introduced the variable of space-time, $\tau = \frac{V}{Q}$. The conversion can be calculated from the concentration of component i in the feed and product stream as such:

$$X_i = \frac{c_i^{in} - c_i}{c_i^{in}}\tag{33}$$

The flowrate, inlet concentration, desired conversion, and reaction rate relate to the reactor volume in this way:

$$Q c_i^{in} X_i = -r_i V\tag{34}$$

$$\frac{X_i}{\tau} = -\frac{r_i}{c_i^{in}}\tag{35}$$

3.3 Plug flow reactor(PFR)

While a PFR is assumed to be perfectly mixed radially, there is assumed to be no mixing along the length of the pipe. The reaction rate is therefor dependent on the position, and the mole balance has to be written as follows:

$$\frac{dn_i}{dt} = Q^{in} c_i^{in} - Q c_i + \int_V r_i dV\tag{36}$$

As the reactor is assumed to be well-mixed radially, the reaction rate is only dependent on the position along the length of the reactor, x . If we look at a slice of the reactor of cross-section A and thickness Δx , we can write the mole balance for component i for that section as:

$$\frac{dn_i}{dt} = Q c_i(x) - Q c_i(x + \Delta x) + r_i A \Delta x\tag{37}$$

$$\frac{dc_i}{dt} A \Delta x = -Q (c_i(x + \Delta x) - c_i(x)) + r_i A \Delta x\tag{38}$$

If we let the thickness of the slice go to zero, we obtain:

$$A \frac{\partial c_i}{\partial t} = -Q \frac{\partial c_i}{\partial x} + r_i A\tag{39}$$

$$\frac{\partial c_i}{\partial t} = -v \frac{\partial c_i}{\partial x} + r_i\tag{40}$$

where $v = \frac{Q}{A}$ is the fluid velocity in the reactor. As this is a partial differential equation, we need the initial and boundary conditions. These are

$$c_i = c_i^0 \quad \text{for} \quad t = 0 \quad \text{and} \quad 0 < x < L \quad (41)$$

$$c_i = c_i^{in} \quad \text{for} \quad t > 0 \quad \text{and} \quad x = 0 \quad (42)$$

When considering the plug flow reactor in steady-state, the dependence on time disappears, and we get

$$r_i = v \frac{dc_i}{dx} = \frac{dc_i}{d\vartheta} = Q \frac{dc_i}{dV} \quad (43)$$

where $\vartheta = \frac{x}{v}$ is a residence time dependent on the position along the reactor length.

4 Design of ideal reactors for first-order reactions

In this section we will see how to use the principles above to design CSTR and PFR reactors under isothermal conditions and only considering a single, irreversible, first-order reaction:



Under the assumed conditions we can write the rate of reaction as

$$r = kc_A \quad \text{or} \quad r_A = -kc_A \quad (45)$$

Recall that because A is a reactant, its stoichiometric coefficient ν is negative (in this case -1).

4.1 CSTR

Applying this equation in the rate for a CSTR, we can rewrite equation 32 as

$$\begin{aligned} c_A - c_A^{in} &= r_A \tau = -kc_A \tau \\ c_A^{in} &= c_A (1 + k\tau) \\ c_A &= \frac{c_A^{in}}{1 + k\tau} \end{aligned} \quad (46)$$

here, the product $k\tau$ is also known as the first *Damköhler number*, denoted as Da . It can be used to give a rough estimate of the conversion that can be expected given a known rate constant and residence time:

$$\begin{aligned} X_A &= \frac{c_A^{in} - c_A}{c_A^{in}} \\ &= \frac{c_A^{in} - \frac{c_A^{in}}{1+k\tau}}{c_A^{in}} \\ &= 1 - \frac{1}{1+k\tau} \\ &= \frac{k\tau}{1+k\tau} \end{aligned} \quad (47)$$

This way it is fairly simple to estimate that for a first Damköhler number of 0.1, the conversion is less than 0.1, while for a value of 10 it is over 0.9. Equation 46 can also be rewritten to render the volume of the reactor as a function of the flowrate, reaction rate constant, and conversion:

$$\begin{aligned} c_A^{in} - c_A &= kc_A \tau = kc_A \left(\frac{V}{Q} \right) \\ V &= \frac{Q (c_A^{in} - c_A)}{kc_A} \\ V &= \frac{Q}{k} \left(\frac{c_A^{in}}{c_A} - 1 \right) = \frac{Q X_A}{k (1 - X_A)} \end{aligned} \quad (48)$$

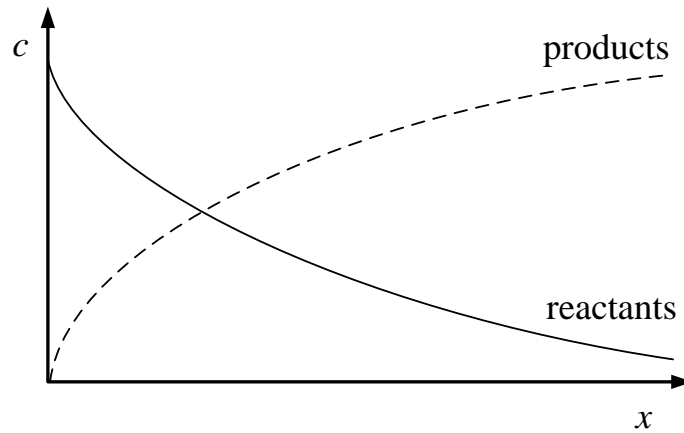


Figure 5: concentration profile along the length of a plug flow reactor

4.2 PFR

Similarly, the reaction rate can be substituted into equation 43 for a PFR to yield

$$Q \frac{dc_A}{dV} = -kc_A$$

and since $c_A = c_A^{in}$ for $x = 0$,

$$c_A = c_A^{in} e^{-\frac{k}{Q}V} \quad (49)$$

$$\frac{c_A}{c_A^{in}} = 1 - X_A = e^{-k\tau}$$

$$X_A = 1 - e^{-k\tau} \quad (50)$$

the assumptions made in the design of the PFR cause each differential volume of the reactor to behave like a batch reactor as it moves through the pipe. As a result, the concentration profile along the length of a PFR looks much like the concentration profile in a batch reactor over time, as seen in Figure 5. One can also solve for the volume of reactor necessary to achieve a desired conversion, starting from equation 49:

$$\frac{c_A^{in}}{c_A} = e^{\frac{k}{Q}V}$$

$$V = \frac{Q}{k} \ln \left(\frac{c_A^{in}}{c_A} \right) = \frac{Q}{k} \ln \left(\frac{1}{1 - X_A} \right) \quad (51)$$

4.3 Comparison of CSTR and PFR

In general, reactions tend to exhibit kinetics of positive order, meaning that as the reactants are consumed the rate of reaction decreases. As a CSTR is already at the composition of the product, the reactants are already consumed, and their concentration is low. Consequently, the CSTR typically has a larger volume than a PFR that reaches the same conversion. For the reaction considered above, Figure 6b compares the volumes of both types of reactors.

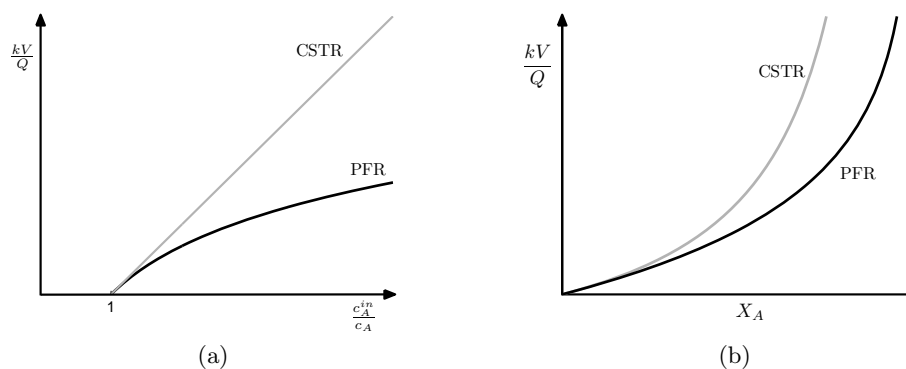


Figure 6: Comparison of reactor volume for CSTR and PFR for various $\frac{c_A^{in}}{c_A}$ (a) and X_A (b)

5 Dynamic behavior of CSTR during start-up

So far we have looked at the steady-state operation of reactors. But when a CSTR is started up it undergoes a transitional period until it reaches that steady-state. How does the concentration in the reactor behave during this time period, and how long does it take to get reasonably close to the steady-state? To answer this, we go back to the mole balance from equation 32, but we no longer assume the number of moles of component i to be constant. We still assume, however, that the reactor is well-mixed and isothermal, and that the volume is constant (so $Q^{in} = Q$). Considering the reaction from before:



we obtain

$$\begin{aligned} \frac{dn_A}{dt} &= V \frac{dc_A}{dt} = Qc_A^{in} - Qc_A + r_A V \\ \frac{dc_A}{dt} &= \frac{1}{\tau} c_A^{in} - \frac{1}{\tau} c_A - kc_A \end{aligned} \quad (53)$$

where τ is constant. Equation 53 is a linear inhomogeneous ordinary differential equation.

$$\frac{dc_A}{dt} + \left(k + \frac{1}{\tau}\right) c_A = \frac{1}{\tau} c_A^{in} \quad (54)$$

The integral of the homogeneous part and the particular solution are, respectively,

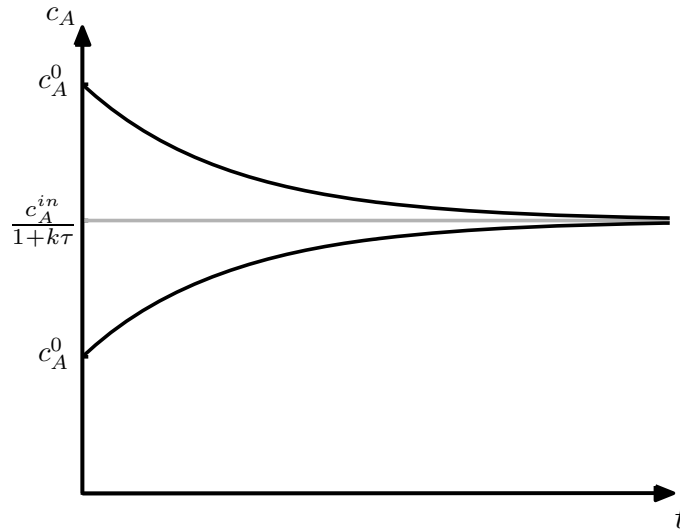
$$c_A^h = A e^{-(k + \frac{1}{\tau})t} \quad (55)$$

$$c_A^p = \frac{c_A^{in}}{1 + k\tau} \quad (56)$$

By applying the initial condition $c_A(0) = c_A^0$ we obtain

$$c_A = \left(c_A^0 - \frac{c_A^{in}}{1 + k\tau}\right) e^{-\left(\frac{1+k\tau}{\tau}\right)t} + \frac{c_A^{in}}{1 + k\tau} \quad (57)$$

Note that if you take this solution and find the limit as $t \rightarrow \infty$ you arrive at equation 46, the steady-state condition. See Figure 7 for an example of the evolution of concentration in a CSTR during start-up.

Figure 7: concentration of reactant A in a CSTR during start-up

6 Reversible reactions

6.1 Material balance for reversible reaction

Until now we have only considered irreversible reactions, where reactants form products, but not the other way around. In reality, many reactions can go both ways, even if one side of the equation might be strongly favored over the other one. Let us consider now a general reversible reaction:



where the forward reaction is governed by the rate constant k_1 and the reverse reaction by the rate constant k_2 . The overall reaction rate is then the difference between the rate of consumption of A and the rate of its production.

$$r = k_1 c_A - k_2 c_B \quad (59)$$

Given enough time this system will settle in an equilibrium that depends on the two rate constants. At this point there is no net reaction, so the concentration of the reactant and the products can be related to each other through the two rate constants:

$$r = 0 \quad (60)$$

$$\frac{c_B}{c_A} = \frac{k_1}{k_2} = K \quad (61)$$

where $K = \frac{k_1}{k_2}$ is the *equilibrium constant* for this reaction under these conditions. You may recall this constant from earlier in the semester when it was found through the Gibbs free energy of formation ΔG_r^0 in the thermodynamics script. To find the concentration of the reactant in a CSTR for a reversible reaction, start at Equation 32:

$$c_A - c_A^{in} = r_A \tau = (-k_1 c_A + k_2 c_B) \tau \quad (62)$$

and

$$c_B - c_B^{in} = r_B \tau = (k_1 c_A - k_2 c_B) \tau$$

Further, since mass is conserved,

$$\begin{aligned} c_A + c_B &= c_A^{in} + c_B^{in} \\ c_B &= c_A^{in} + c_B^{in} - c_A \end{aligned} \quad (63)$$

Rewriting Equation 62, we get

$$\begin{aligned} c_A (1 + k_1 \tau) - k_2 \tau c_B &= c_A^{in} \\ c_A (1 + k_1 \tau) &= c_A^{in} + k_2 \tau c_B \\ &= c_A^{in} + k_2 \tau (c_A^{in} + c_B^{in} - c_A) \\ c_A (1 + k_1 \tau + k_2 \tau) &= c_A^{in} + k_2 \tau (c_A^{in} + c_B^{in}) \\ c_A &= \frac{c_A^{in} + k_2 \tau (c_A^{in} + c_B^{in})}{1 + \tau (k_1 + k_2)} \end{aligned} \quad (64)$$

and similarly for component B

$$c_B = \frac{c_B^{in} + k_1 \tau (c_A^{in} + c_B^{in})}{1 + \tau (k_1 + k_2)} \quad (65)$$

For a reversible reaction, there is a limit to the conversion, set by the equilibrium. If you had an infinitely large CSTR, $\tau \rightarrow \infty$, and

$$c_A = \frac{k_2 (c_A^{in} + c_B^{in})}{k_1 + k_2} = \frac{c_A^{in} + c_B^{in}}{1 + K} \quad (66)$$

c_A , and as a result the conversion X , depends on both the inlet concentration of component A and B. Assuming that you are only feeding your reactant (and $c_B^{in} = 0$), the limit to the conversion is found to be

$$X = \frac{c_A^{in} - c_A}{c_A^{in}} = \frac{c_A^{in} - \frac{c_A^{in}}{1+K}}{c_A^{in}} = 1 - \frac{1}{1+K} = \frac{K}{1+K} \quad (67)$$

6.2 Equilibrium-limited reactions

The conversion at equilibrium depends on the equilibrium constant, which in turn depends on the temperature:

$$K = e^{-\frac{\Delta G^0(T)}{RT}} \quad (68)$$

Figure 8 shows how the equilibrium conversion changes with temperature. Especially for exothermic reactions this is a concern. To achieve high reaction rates a high temperature is needed, but this can severely lower the conversion. Not only does the equilibrium pose a limit to the conversion, even getting close to it takes a high toll on reaction rate. There are different attempts to circumvent this, such as using higher pressures, as we will see in the next section, or using tanks in series, as we will see later.

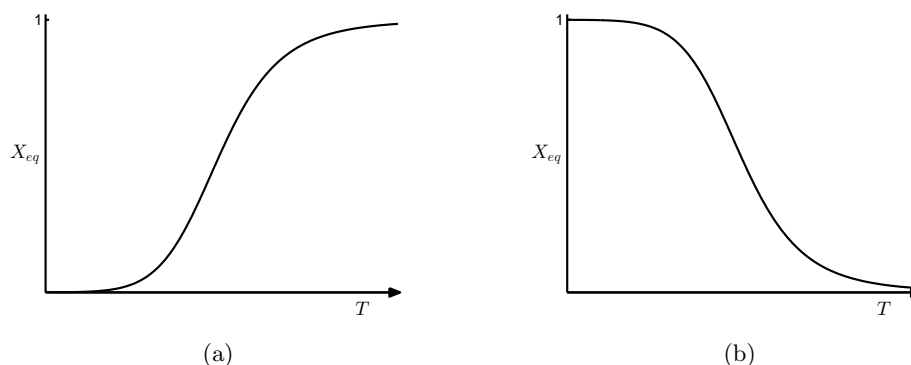


Figure 8: Equilibrium conversion dependency on temperature for an edothermic (a) and an exothermic (b) reaction.

7 Thermodynamics of chemical equilibrium

Consider a single reaction occurring in a batch reactor. The rate of change of the amount of any component i in the reactor is given by

$$\begin{aligned}\frac{dn_i}{dt} &= \nu_i r V \\ dn_i &= \nu_i r V dt = \nu_i d\lambda\end{aligned}\quad (69)$$

where $d\lambda = rVdt$ is the *extent of reaction*. For multiple reactions then, the differential change of the amount of i is given by the sum over all reactions j ,

$$dn_i = \sum_j \nu_{ij} d\lambda_j \quad (70)$$

If we now consider a system at a given temperature T and pressure P , then

$$dG = \sum_i \mu_i dn_i = \left(\sum_i \mu_i \nu_i \right) d\lambda \quad (71)$$

and at equilibrium

$$dG = 0 \Leftrightarrow \sum_i \mu_i \nu_i = 0 \quad (72)$$

Now take an ideal gas mixture in this system, in which a reaction is taking place, e.g. $A + B \rightleftharpoons C + D$. Then

$$\mu_i^*(T, P, \underline{y}) = \mu_i^*(T, P_r) + RT \ln \left(\frac{P_i}{P_r} \right)^{\nu_i} \quad (73)$$

$$\begin{aligned}0 &= \sum_i \nu_i \mu_i^*(T, P, \underline{y}) = \sum_i \nu_i \mu_i^*(T, P_r) + RT \sum_i \ln \left(\frac{P_i}{P_r} \right)^{\nu_i} \\ &= \sum_i \nu_i \mu_i^*(T, P_r) + RT \ln \prod_i \frac{(P y_i)^{\nu_i}}{P_r^{\nu_i}} \\ &= \Delta G^0(T, P_r) + RT \ln \left[\left(\frac{P}{P_r} \right)^{\sum_i \nu_i} \prod_i y_i^{\nu_i} \right]\end{aligned}\quad (74)$$

where $\Delta G^0(T, P_r) = \sum_i \nu_i \mu_i^*(T, P_r)$. Rearranging the equation gives us

$$\underbrace{\left(\frac{P}{P_r}\right)^{\sum_i \nu_i} \prod_i y_i^{\nu_i}}_{Q(P,y)} = \underbrace{\exp\left(-\frac{\Delta G^0(T)}{RT}\right)}_{K_{eq}(T)} \quad (75)$$

The right-hand-side of this equation is the equilibrium constant for the reaction, as we have seen before. While these quantities are equal in equilibrium, they are not when the system is not in equilibrium:

$$\begin{array}{llll} Q(P, y) = K_{eq}(T) & \Rightarrow & dG = 0 & \text{no reaction} \\ Q(P, y) > K_{eq}(T) & \Rightarrow & dG > 0 & \text{A + B} \longleftarrow \text{C + D} \\ Q(P, y) < K_{eq}(T) & \Rightarrow & dG < 0 & \text{A + B} \longrightarrow \text{C + D} \end{array}$$

Consider now once again the reaction of nitrogen and hydrogen forming ammonia (Equation 1). Applying Equation 75 gives us the following relationship:

$$K_{eq}(T) = P_r^2 \frac{P^2 y_{\text{NH}_3}^2}{P^4 y_{\text{N}_2} y_{\text{H}_2}^3} = \frac{P_r^2 y_{\text{NH}_3}^2}{P^2 y_{\text{N}_2} y_{\text{H}_2}^3} \quad (76)$$

This shows that while the equilibrium constant K_{eq} is a function of temperature, the pressure of the system also affects the composition at the equilibrium. In the above reaction, NH_3 is desired, so it is of interest to increase the mole fraction of it at equilibrium. As we saw earlier in Section 1.1 a low temperature would favor ammonia. This would, however, severely lower the reaction rate. To get a higher conversion despite the high temperature, then, the pressure can be increased.

$$\begin{array}{llll} P \uparrow & \Rightarrow & y_{\text{NH}_3} \uparrow & \Rightarrow \text{good!} \\ P \downarrow & \Rightarrow & y_{\text{NH}_3} \downarrow & \Rightarrow \text{bad!} \end{array}$$

8 Energy balance of a CSTR

8.1 The general energy balance

Consider again a CSTR in steady state, meaning all derivatives in time are zero. This reduces the energy balance from Equation 23 to

$$0 = -UA(T - T_a) + Q^{in} \left(\sum_i c_i^{in} c_{p,i} \right) (T^{in} - T) + Vr(-\Delta H_r) \quad (77)$$

This can be rewritten as (note that we consider $Q^{in} = Q^{out} = Q$)

$$\begin{aligned} UA(T - T_a) + Q^{in} \left(\sum_i c_i^{in} c_{p,i} \right) (T - T^{in}) &= Vr(-\Delta H_r) \\ \frac{UA}{Q}(T - T_a) + \left(\sum_i c_i^{in} c_{p,i} \right) (T - T^{in}) &= \tau r(-\Delta H_r) \\ \sum_i c_i^{in} c_{p,i} \left[\frac{UA}{Q(\sum_i c_i^{in} c_{p,i})} (T - T_a) + T - T^{in} \right] &= \tau r(-\Delta H_r) \end{aligned} \quad (78)$$

We now define two new variables:

$$\beta = \frac{UA}{Q(\sum_i c_i^{in} c_{p,i})} \quad (79)$$

$$T_c = \frac{T^{in} + T_a \beta}{1 + \beta} \quad (80)$$

This allows us to rewrite the above as

$$\begin{aligned} \sum_i c_i^{in} c_{p,i} [T(1 + \beta) - T^{in} - T_a \beta] &= \tau r(-\Delta H_r) \\ \underbrace{\sum_i c_i^{in} c_{p,i} [(1 + \beta)(T - T_c)]}_{\text{heat removed } R(T)} &= \underbrace{\tau r(-\Delta H_r)}_{\text{heat generated } \tilde{G}(T, c_A)} \end{aligned} \quad (81)$$

Note that the two new variables are not arbitrary: β relates the influence on the reactor temperature of the heat exchanger to that of the entering feed, and T_c is an intermediate temperature between the feed temperature and the temperature of the heat transfer fluid, i.e. it is a weighted average of the two.

The two sides of Equation 81 are the heat removed from the reactor and the heat generated by the reaction, respectively. They represent the energy balance for a CSTR at steady-state, as a function of three groups of parameters: The feed conditions (c_i^{in} , T^{in}), the reactor cooling characteristics (T_c and β), and the residence time ($\tau = \frac{V}{Q^{in}}$). The heat removed $R(T)$ (left-hand side) depends only on two parameters, namely β and T_c ; the effect that each of these parameters has on the removed heat is shown in Figure 9. The heat generated is not only a function of the reactor temperature, but also of the reaction rate, which depends on the reactant concentration at steady state.

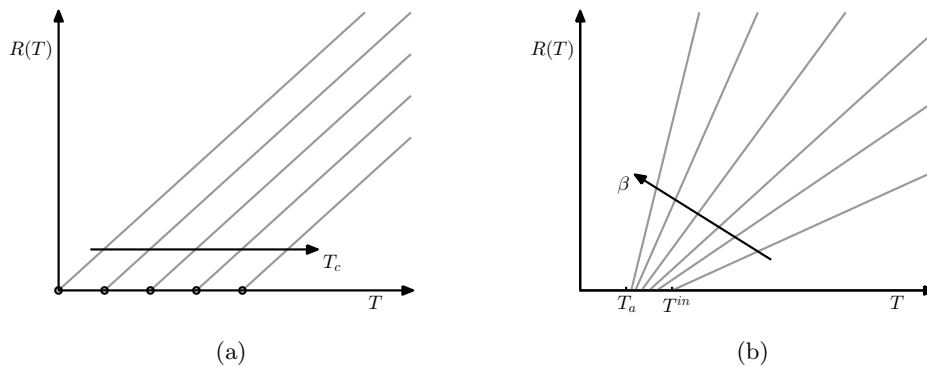
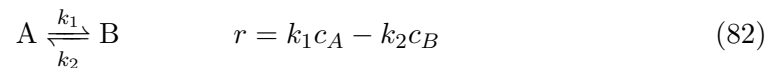
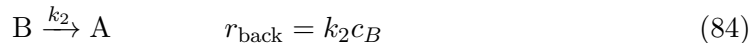
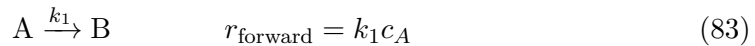


Figure 9: The heat removal rate from a CSTR changes with T_c , the intermediate temperature of the heat transfer fluid and the feed, as seen in (a) and on the value of β as seen (b)

Reversible Reactions As we saw in Section 6, chemical reactions are often reversible, meaning they can go in both directions:



Alternatively, they can be considered as two entirely separate reactions as such:



If the heat of reaction for these two reactions are ΔH and ΔH_{back} , respectively, then $\Delta H_{\text{back}} = -\Delta H$. This leads to the following expression for the net rate of heat generation $\left[\frac{\text{J}}{\text{m}^3 \text{s}}\right]$:

$$r_{\text{forward}} \Delta H + r_{\text{back}} \Delta H_{\text{back}} = (r_{\text{forward}} - r_{\text{back}}) \Delta H \quad (85)$$

$$= (k_1 c_A - k_2 c_B) \Delta H \quad (86)$$

Here it is obvious that the reaction rate for the combined reactions is the same as the one for the reversible reaction (Equation 82). This means that with regard to the energy balance of a reactor (see Equation 81), all the considerations concerning a single, irreversible reaction can be applied to a reversible reaction, provided that the appropriate rate expression from Equation 82 is used. Further, recall from Equation 63 that c_B can be expressed as a function of the initial concentrations and c_A , so the net heat generated depends on c_A only:

$$(k_1 c_A - k_2 c_B) \Delta H = (k_1 c_A - k_2 (c_A^{\text{in}} + c_B^{\text{in}} - c_A)) \Delta H = \frac{\tilde{G}(T, c_A)}{\tau} \quad (87)$$

8.2 Steady-state in a CSTR with an exothermic reaction

Consider now an exothermic, irreversible reaction with a single reactant taking place in a cooled CSTR.



The energy and mass balances for a CSTR at steady state are then given by:

$$\begin{cases} R(T) = \tilde{G}(T, c_A) = \tau(-\Delta H)r(T, c_A) \\ c_A^{in} - c_A = \tau r(T, c_A) = \tau c_A k(T) \end{cases} \quad (89)$$

Note that the second equation is Equation 32, and that by solving it with respect to c_A , one obtains Equation 46. Therefore the system (89) can be rewritten as:

$$\begin{cases} c_A = \frac{c_A^{in}}{1 + \tau k(T)} \\ R(T) = \tilde{G}(T, c_A) = (-\Delta H)c_A^{in} \left(\frac{\tau k(T)}{1 + \tau k(T)} \right) = G(T) \end{cases} \quad (90)$$

Therefore the concentration of A can be expressed as a function of T through $k(T)$, and the heat generated is given as solely a function of temperature, with parameters τ and ΔH . The effect of these parameters on the heat generation curve is shown in Figure 10.

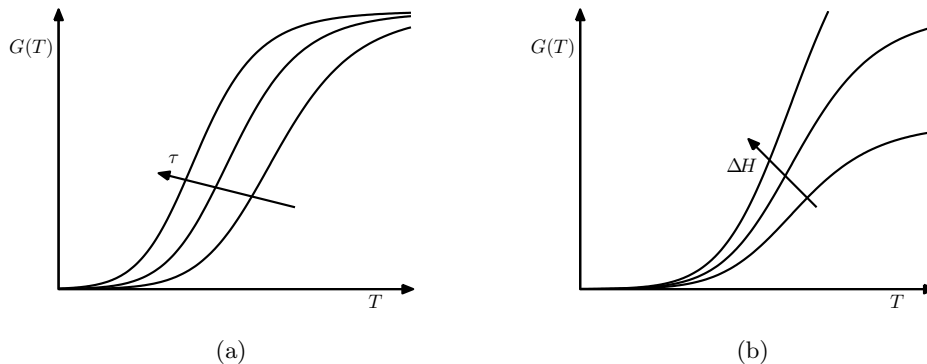


Figure 10: The generation of heat from the reaction depends strongly on the temperature of the reactor, the residence time (as seen in (a)), and on the heat of reaction (seen in (b)).

8.2.1 Stability of steady-states

For the reactor to be at steady-state, $R(T) = G(T)$. Figure 11 shows three heat removal lines together with a heat generation line, and highlights the steady-states. At any other temperature, the behavior of the reactor depends on the relationship between the two lines:

$$\begin{array}{ll} R(T) > G(T) & \text{reactor cools off} \\ R(T) = G(T) & \text{steady-state} \\ R(T) < G(T) & \text{reactor heats up} \end{array}$$

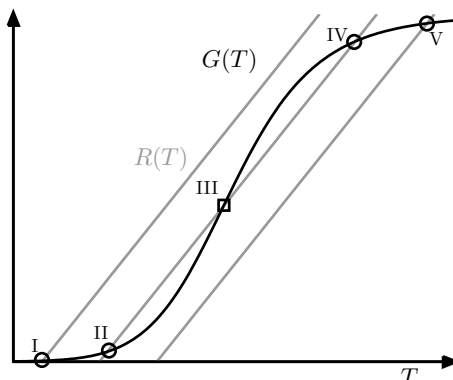


Figure 11: The roman numerals I-V denote steady-states. The circles are stable, while the square is an unstable steady-state.

In Figure 11, for example, if the reactor is operated between points III and IV using the middle value of T_c , the heat generation is higher than the removal, leading the reactor to heat up. Once the temperature passes point IV, however, more heat is removed than is generated, causing the reactor to cool off. This is why point IV is considered a *stable* steady state: A small deviation in temperature in either direction will cause the system to self-correct and return to the steady-state. Point III, meanwhile, is an *unstable* steady state. If the reactor is operated at that temperature, it will neither heat up nor cool off, and is at steady state. If, however, there is a small disturbance that warms the reactor a little bit, the heat generated will outweigh the removed heat, and the reactor will heat up further and further. A small disturbance to a lower temperature will have the opposite effect: The now prevalent heat removal will cool the reactor off more and more.

What it comes down to is that if the derivative of the heat removal line at the steady state is higher than the heat generation line, the steady state is stable; if it is lower, the steady state is unstable.

8.2.2 Multiplicity of steady states, ignition and extinction temperatures

As you can see in Figure 11, the middle heat removal line allows for three distinct steady states. This is called a multiplicity of steady states. As III is an unstable steady state, the reactor would not remain there for a long period of time. Whether the reactor runs at point II or at IV depends on its starting point. At any temperature below III it will settle on point II, at any higher temperature it will end up at IV. If T_c changes a little, the reactor temperature will change accordingly, but remain in the same region. Only if T_c changes past the ignition temperature will the reactor be forced to go to the high temperature. Conversely, if the temperature drops below the extinction temperature, the reactor drops to cool temperatures, as seen in Figure 12

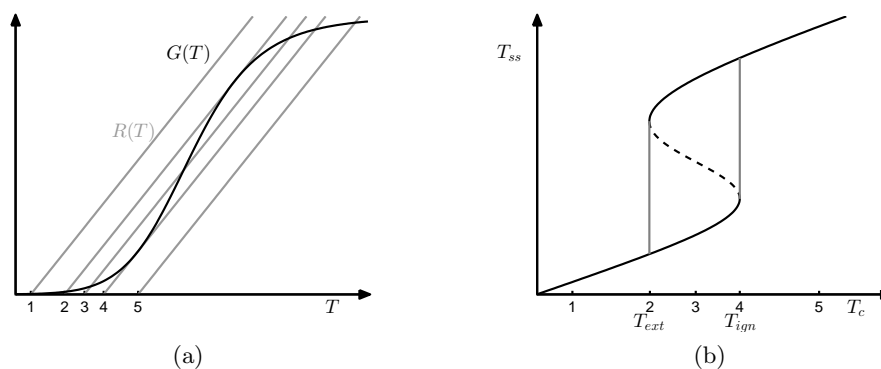
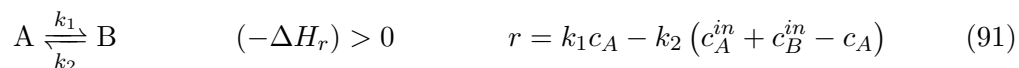


Figure 12: (a) shows a curve of heat generation along with five possible heat removal lines. 1 and 5 have only one steady-state. 3 has two stable steady states. Which one the reactor is at depends on the initial temperature. 2 and 4 are the extinction and ignition temperatures, respectively. (b) shows the steady state reactor temperature for a range of T_c , including the five temperatures seen in (a), clearly showing the region with two possible operating conditions

8.3 Adiabatic CSTR

8.3.1 Equilibrium limit in an adiabatic CSTR

Reactions are also frequently carried out in a vessel that is neither heated nor cooled, with the heating/cooling taking place either upstream or downstream of the reactor. As a result, these reactors are adiabatic and modeled as such. We will now look at an adiabatic CSTR in which an exothermic, reversible reaction is taking place.



We have seen in section 6.2 that this exothermic reaction will be limited by its equilibrium. In section 8.1 then we saw that the temperature in the reactor depends on the heat generated and the heat removed. The energy and mass balances are repeated here:

$$\begin{cases} \overbrace{\sum_i c_i^{in} c_{p,i} (1 + \beta) (T - T_c)}^{\text{heat removed } R(T)} = \overbrace{\tau r(T, c_A) (-\Delta H_r)}^{\text{heat generated } \tilde{G}(T, c_A)} \\ c_A^{in} - c_A = \tau r(T, c_A) = X_A c_A^{in} \end{cases} \quad (92)$$

where we exploit the definition of conversion X_A , i.e. $X_A = \frac{c_A^{in} - c_A}{c_A^{in}}$. In an adiabatic CSTR, $\beta = 0$ and $T_c = T^{in}$. As a result, substituting the second equation into the first yields:

$$\left(\sum_i c_i^{in} c_{p,i} \right) (T - T^{in}) = c_A^{in} X_A (-\Delta H_r) \quad (93)$$

In this last equation, the left-hand side is the heat removed through the cooling effect of the incoming feed, and the right-hand side is the heat produced by the reaction. Equation 93 describes a linear relationship between the conversion and the temperature in the reactor.

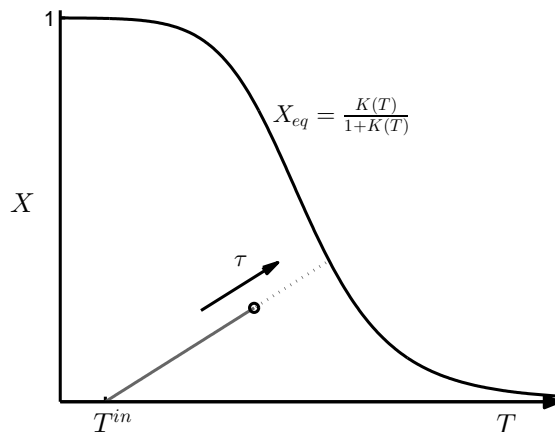


Figure 13: Conversion and temperature in the reactor have a linear relationship. The only influence that the residence τ has is that it determines where along the line the reactor is operated.

While it does not provide the steady-state conditions of the reactor directly, it describes a path along which the operating point of the reactor can be found for any given residence time τ . One can solve the system 92 numerically to find the temperature and conversion of the reaction for any given residence time.

Consider now a reactor where the feed is pure A (so $c_B^{in} = 0$). Substituting the reaction rate given in Equation 91 into the mass balance in system 92 yields Equation 64 for c_A

$$c_A = \frac{c_A^{in} + k_2\tau (c_A^{in})}{1 + \tau (k_1 + k_2)} \quad (94)$$

This equation can be substituted for c_A in the second equation in (92), which when substituted into the first equation, yields the relationship between the temperature in the reactor and the residence time as

$$\left(\sum_i c_i^{in} c_{p,i} \right) (T - T^{in}) = c_A^{in} (-\Delta H_r) \frac{k_1(T)\tau}{1 + \tau (k_1(T) + k_2(T))} \quad (95)$$

Here again one can use the definition of the conversion $X_A = \frac{c_A^{in} - c_A}{c_A^{in}} = \frac{\tau k_1}{1 + \tau (k_1 + k_2)}$, where $k_1 = k_1(T)$ and $k_2 = k_2(T)$. The conversion in the reactor can be taken to two limits, infinite τ and infinite temperature, with the following results:

$$X_A \begin{cases} \rightarrow \frac{K(T)}{1+K(T)} & \text{when } \tau \rightarrow \infty \\ \rightarrow \frac{\tau k_{1,\infty}}{1+\tau(k_{1,\infty}+k_{2,\infty})} & \text{when } T \rightarrow \infty \end{cases} \quad (96)$$

where $k_{1,\infty}$ and $k_{2,\infty}$ are the limits of the two rate constant for infinite temperature. As was shown before, the conversion does not go to 1 for an infinite τ , but approaches the equilibrium limit, as is shown in Figure 13.

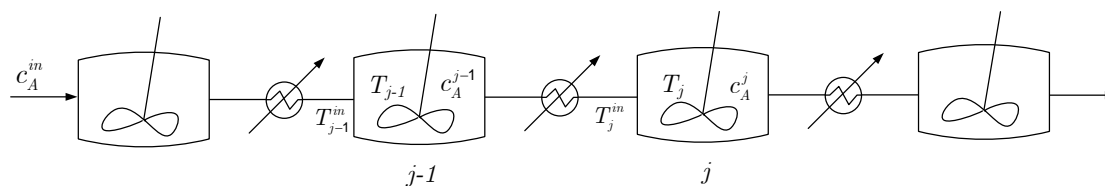


Figure 14: Several CSTRs in series. The product from each reactor is cooled to move away from the equilibrium limit, and then fed to the next reactor. As reactors often contain a catalyst without which the reaction does not progress, it is typically assumed that the feed entering reactor j is of the same composition as the product from $j - 1$ (i.e. $c_A^{in,j} = c_A^{j-1}$)

8.3.2 Multiple reactors in series

As you could see in Figure 13, the equilibrium limit for conversion might still be relatively low. By cooling the reactor a lower temperature can be maintained for higher conversions, however it is often more efficient to use a dedicated heat exchanger to cool the streams. If the product from the reactor is cooled, it can be fed to another reactor, where it can continue to react. See Figure 14 for a schematic.

In this system, c_A^{in} and c_B^{in} refer to the concentrations of A and B in the feed entering the first reactor. The concentrations entering all subsequent reactors are equal to the outlet concentrations from the previous reactor, so

$$c_A^{in,j} = c_A^{j-1} \quad \text{and} \quad c_B^{in,j} = c_B^{j-1} \quad (97)$$

For obvious reasons, the conversion in reactor j is not calculated on the basis of the feed entering it, but on the initial feed. As a result, as c_A decreases throughout the reactor cascade, the conversion increases with each reactor:

$$X_A = \frac{c_A^{in} - c_A^j}{c_A^{in}} \quad (98)$$

$$X_A^1 < X_A^2 < \dots < X_A^{j-1} < X_A^j < \dots \quad (99)$$

For each reactor in the cascade, Equation 93 becomes

$$\begin{aligned} \left(\sum_i c_i^{in} c_{p,i} \right) (T_j - T_j^{in}) &= \tau_j r_j (-\Delta H_r) \\ &= (c_A^{j-1} - c_A^j) (-\Delta H_r) \\ &= c_A^{in} (X_A^j - X_A^{j-1}) (-\Delta H_r) \\ \frac{(\sum_i c_i^{in} c_{p,i})}{(-\Delta H) c_A^{in}} (T_j - T_j^{in}) &= X_A^j - X_A^{j-1} \end{aligned} \quad (100)$$

So for each reactor, the conversion and temperature are linearly related, and both a function of τ . A series of CSTRs with interstage cooling can achieve higher conversion than a single reactor, while remaining at reasonably high temperatures. A schematic of the conversion for a five reactor cascade is illustrated in Figure 15, where five reactors in series with intermediate cooling produce a sawtooth wave pattern to high conversion. Note

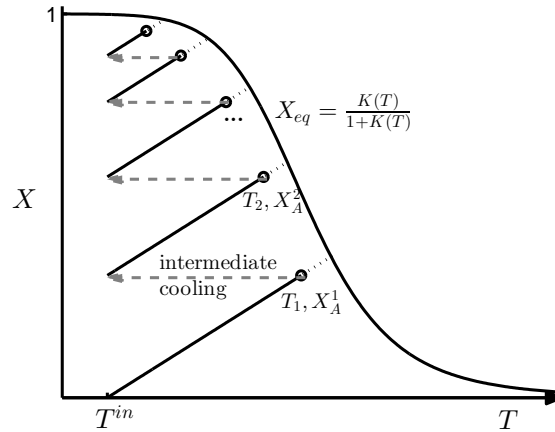


Figure 15: Several CSTRs in series. The product from each reactor is cooled to move away from the equilibrium limit, and then fed to the next reactor.

that Equation 100 does not give the reactor conditions at steady state, but describes a line along which the operating conditions depend on τ . In the design of the reactor cascade one has to consider the inherent trade-off: A higher conversion in each reactor requires a larger τ , however as the equilibrium limit is approached the increase in conversion becomes smaller for an increase in τ (and therefore reactor size). Interstage cooling can be used to move away from the equilibrium limit, allowing the reaction to proceed further in the next reactor. This allows a step-wise approach to higher conversion at the expense of the amount of necessary equipment (reactors, heat exchangers, etc.).