Chemical Reaction Engineering - Part 12 - multiple reactions

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Multiple reactions are usually present

So far we have considered reactors in which only one reaction is present. However, in almost all cases, there will be other reactions present. Examples include degradation of our reactant and desired products into undesired decomposition products, and reactions that deactivate a catalyst.

During petroleum refining reactions, decomposition of hydrocarbons to form a carbonaceous solid called "coke" can occur. Coke deposits decrease heat exchange coefficients on reactor walls and can deactivate catalysts. Coke deposition can be inhibited by increasing hydrogen pressure, for example.

During partial oxidation of hydrocarbons, complete oxidation of reactants and products must be inhibited. An example of a partial oxidation reaction, also called a selective oxidation reaction, is the partial oxidation of ethylene to ethylene oxide over selective supported silver catalysts.

In order to keep things simple, we will consider the presence of only one or two reactions in addition to the main reaction that produces our desired product.

Our goal is maximum production of the desired product and minimum production of the undesired products.

Our tools to accomplish this goal include designing to achieve the best reactant concentrations, the best temperature or temperature progression, and the best feed or removal rates if we use a semi-batch reactor.

Classification of multiple reaction systems

We can't always fit reaction systems into these classifications but you should know the terms and what they mean.

Series reaction system: A → D → U   or   A → U → D

where D is the desired product and U is the undesired product.

Parallel reaction system: A → D
                                 A → U

Series-parallel system: A → D → U   plus   A → U

Independent reactions: A → D
                                 B → U

Selectivity and yield

Selectivity and yield are two quantitative measures of how well we achieve the goal of maximizing production of D and minimizing production of U.

Warning: Whenever you encounter these words, double check how the author is using the terms. Unfortunately, not all authors provide a definition when they use these terms. In some textbooks, the equation used to compute selectivity, for example, may change from example to example without notice and without a definition being provided.

Therefore, whenever <u>you</u> use one of these terms in your own writing, make sure that you state your definition of the terms.

Here we define the instantaneous selectivity *S* as the rate of production of D divided by the rate of production of U at the current time. We define the overall selectivity Ŝ as the moles of D at the end of the reaction divided by the moles of U.

$$S_{DU} = \frac{r_D}{r_U} \quad ; \quad \hat{S}_{DU} = \frac{N_D}{N_U}$$

Here we define the instantaneous yield *Y* as the rate of production of D divided by the rate of production of consumption of A at the current time. We define the overall yield Ŷ as the moles of D at the end of the reaction divided by the moles of A converted.

$$Y_D = \frac{r_D}{-r_A} \quad ; \quad \hat{Y}_D = \frac{N_D}{N_{A0} - N_A}$$

Another definition of overall yield, which you might encounter, is N_D/N_{A0}.

Series reactions

This system is trivial: A → U → D. We simply need to react a long time to convert everything to D.

This system is not trivial: A → D → U. If we react for only a short time, we don't make much D. If we react for too long a time, we end up with mainly U.

The procedure for this non-trivial case is to specify an objective and then solve for the reaction time that achieves that objective. For example, the objective might be to maximize the concentration of D at the end of the reaction.

Be careful. The maximum selectivity and yield are obtained at t = 0+ when the first D has been formed and insignificant U has formed. This is high selectivity and yield but you have almost no D to sell.

You may be asked in a homework or exam problem to find the reaction time to maximize N_D, for example.

In a design problem, you may be able to associate costs with each component: reactor equipment, reactor operation, cost of purchasing A, cost of disposing of U, and price at which you can sell D. With these costs, you can write an "objective function" to maximize: net profit as a function of reaction time (reminder: set derivative of profit with respect to reaction time to zero and solve for reaction time at this condition).

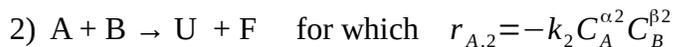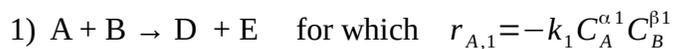Parallel reactions - Case 1

Consider the following case:

     1) A → D   for which $r_{A,1} = -k_1 C_A^{\alpha 1}$

     2) A → U   for which $r_{A,2} = -k_2 C_A^{\alpha 2}$
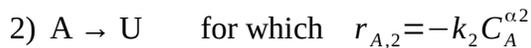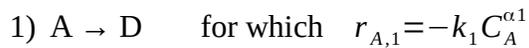
If the order of reaction 1 (α1) > the order of reaction 1 (α2), then you want to start with a high initial concentration of A. For gas-phase reactions, work at relatively high pressure.

If (α1) < (α2), then you want to start with a low initial concentration of A. For liquid-phase reactions, dilute A in a solvent. For gas-phase reactions, work at relatively low pressure. However, the lower the concentration the slower the rate at which you produce D and the larger and more costly your reactor. So this becomes an optimization problem.

If the activation energy of reaction 1 (E1) > the activation energy of reaction 1 (E2), then you want to operate at a relatively high temperature.

If (E1) < (E2), then you want to operate at a relatively low temperature. However, the lower the temperature the slower the rate at which you produce D. So this becomes an optimization problem.

Parallel reactions - Case 2

     1) A + B → D + E   for which $r_{A,1} = -k_1 C_A^{\alpha 1} C_B^{\beta 1}$

     2) A + B → U + F   for which $r_{A,2} = -k_2 C_A^{\alpha 2} C_B^{\beta 2}$

The same argument about activation energies and temperature apply to this case as well as parallel case 1.

There are four possible combinations of reaction orders here.

1) α1 > α2 & β1 > β2
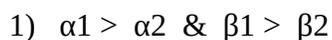
Operate at high initial concentrations of both A and B. For gas-phase reactions, use high gas pressures.

2) $\alpha 1 < \alpha 2$ & $\beta 1 < \beta 2$

Operate at low concentrations of both A and B. Start with dilute A and B in a batch reactor. Or use a semi-batch reactor and feed both A and B into a solvent. For gas-phase reactions, use low gas pressures.

3) $\alpha 1 > \alpha 2$ & $\beta 1 < \beta 2$

Operate at high concentration of A and low concentrations of B. Use a semi-batch reactor and feed B.

4) $\alpha 1 < \alpha 2$ & $\beta 1 > \beta 2$

Operate at low concentration of A and high concentrations of B. Use a semi-batch reactor and feed A.

Component balances - How many?

How many component balances must we write? For a specific system, the number can be determined from a "degrees of freedom" analysis, which you learned about in your material balance course.

For what we call "simple" reactors, which are reactors where the relative numbers of moles of components change only by reaction, the minimum number of component balances is equal to the number of linearly independent stoichiometric equations.

See Part 12-A of these notes, stoichiometry of multiple reactions, for an explanation of how to obtain a set of Independent Stoichiometric Equations (ISE) and extent variables for a multiple reaction system. Also see ReactorLab, Division 5 Multiple Reactions, Lab 1 Stoichiometry for examples.

Batch reactors are simple reactors. As we will see later, Plug Flow Reactors (PFRs) and Continuous Stirred Tank Reactors (CSTRs) are also simple reactors. Semi-batch reactors are complex reactors, not simple in this sense, so we will need to write additional component balances.

The "fall back position" is to write a component balance for every component present. For batch reactors, this results in a differential equation for every component, and these equations must be integrated together, probably using numerical integration.

For single reactions in a simple reactor, we have only been writing one component balance. That is because we use stoichiometry, by writing a stoichiometric table, such that we can write the concentration of any component in terms of initial composition and a conversion variable.

A stoichiometric equation can serve two purposes:

(1) to represent a reaction pathway from specific reactants to specific products via a "reaction mechanism" of "elementary reaction steps,"

and/or

(2) as one of a set of linearly independent mathematical equations that express conservation of elements.

A reaction pathway has an associated rate equation. When we talk about reactions, we are referring to reaction pathways and their stoichiometric equations.

Linearly independent stoichiometric equations can be determined solely from a list of components present and contain no information about kinetics when serving this purpose. An independent stoichiometric equation may also serve in some cases as the stoichiometric equation of a reaction pathway. The number of independent stoichiometric equations may differ from the number of reaction pathways.

Component balances - Options

For multiple reactions, some authors (e.g., Fogler) say to write a component balance for every component present. In this case, you can use concentration or moles (or molar flow rates for PFRs and CSTRs) as variables and don't need conversion or extent variables. This strategy works for simple reactors (batch) and complex reactors (semi-batch).

This is the strategy I recommend for multiple reactions in this introductory course.

This strategy is easy to write and understand and will work for both simple (batch, PFR, CSTR) and complex (semi-batch) reactors. After you obtain a solution in terms of concentration (or moles or molar flow rates), then you can compute any desired conversion, selectivity or yield. For single reactions in a simple reactor, it is obviously more work than necessary because we need to solve only one component balance after we write a stoichiometric table.

For simple reactors, other authors (e.g., Schmidt) say to write a stoichiometric table using a stoichiometric extent variable for each pathway. Then derive differential equations giving the rate of change of each extent variable. This only reduces the number of differential equations when the number of reaction pathways is less than the number of components.

For simple reactors, the minimum number of components balances is equal to the number of independent stoichiometric equations.

A stoichiometric table can be written using these extents. Then write a differential equation giving the rate of change of each extent variable. The advantage of this option is that errors in conservation of elements are eliminated when numerically integrating the ODEs.

Warning: For multiple reactions, do not use conversions to write stoichiometric tables. Defining conversion variables for multiple reactions can get awkward. Using stoichiometric extents to write stoichiometric tables is straightforward. After a solution is obtained in terms of extents, then any conversion values you need are easy to compute.

Stoichiometric table using stoichiometric extent variables

Specify the number of stoichiometric equations j to be used. For each component i, using write this line:

$$N_i = N_{i,0} + \sum_{j=1}^{j=R} \left(\upsilon_i \xi_j \right) \quad ; \quad \begin{array}{l} \upsilon_i = \text{formal stoichiometric coefficient of component } i \\ \xi_j = \text{stoichiometric extent of equation } j \end{array}$$

See the tables in Options 2 and 3 in the Example below.

Example - Series-parallel reaction in batch reactor

We have three reaction pathways. Assume constant volume here. That is not a required assumption, it just allows less typing to write the equations for this example.

$$(1) A \rightarrow D \ , \ r_{A,1} = -k_1 C_A$$
$$(2) D \rightarrow U \ , \ r_{D,2} = -k_2 C_D$$
$$(3) A \rightarrow U \ , \ r_{A,3} = -k_3 C_A$$
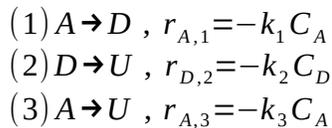
This is a generic representation of a series-parallel system. If we were to translate this into actual chemical components, A, D and U would represent isomers of the same compound. Different isomers are different components as far as reactions and reaction equilibria are concerned. In other examples, their may be other reactant and product components present.

If we were to do a stoichiometric analysis with a specific chemical formula, we would find that there are two independent stoichiometric equations. For example,

A = D and D = U

is a valid set. Through a linear operation (adding the two) we could get another valid independent set.

A = D and A = U

Option 1 - write a component balance for every component

$$\frac{dC_A}{dt} = r_A = -k_1 C_A - k_3 C_A$$

$$\frac{dC_D}{dt} = r_D = k_1 C_A - k_2 C_D$$

$$\frac{dC_U}{dt} = r_U = k_2 C_D + k_3 C_A$$

This is the recommended strategy for multiple reactions in this introductory course.

This strategy is easy to write and understand and will work for both simple (batch, PFR, CSTR) and complex (semi-batch) reactors. For single reactions, it is obviously more work than necessary because we only need to solve one component balance after we write a stoichiometric table.

Option 2 - use an extent variable for each reaction pathway

Write a stoichiometric table using an extent variable for each of the three reaction pathways.

$$N_A = N_{A,0} - \xi_1 \quad - \xi_3$$
$$N_D = N_{D,0} + \xi_1 - \xi_2$$
$$N_U = N_{U,0} \quad + \xi_2 + \xi_3$$

from writing for each component $\quad N_i = N_{i,0} + \sum_{j=1}^{j=R} (\upsilon_i \xi_j)$

For constant volume

$$C_A = C_{A,0} - \xi'_1 \quad - \xi'_3$$
$$C_D = C_{D,0} + \xi'_1 - \xi'_2$$
$$C_U = C_{U,0} \quad + \xi'_2 + \xi'_3$$

where $\quad \xi'_i = \xi_i / V$

Now write an equation for the rate of change of each pathway's extent.

$$\frac{d\xi_1}{dt} = r_1 = k_1 (C_{A,0} - \xi'_1 - \xi'_3)$$

$$\frac{d\xi_2}{dt} = r_2 = k_2 (C_{D,0} + \xi'_1 - \xi'_2)$$

$$\frac{d\xi_3}{dt} = r_3 = k_3 (C_{A,0} - \xi'_1 - \xi'_3)$$

We can integrate these three equations to get ξ'_1 , ξ'_2 and ξ'_3 at any time, then use the stoichiometric table to get concentrations of all three components.

Since the number of reaction pathways in this example equals the number of components, you get the same number of ODEs to integrate with both Option 1 and 2 for this example,. Thus, Option 1 is quicker to write and program for this system. For other reaction systems, the number of reaction pathways may be less than the number of components.

Option 3 - use an extent variable for each independent stoichiometric equation (ISE)

Choose this set of ISE: (1) A = D and (2) D = U

Write a stoichiometric table using an extent variable for each of the two ISE.

$$N_A = N_{A,0} - \xi_1$$
$$N_D = N_{D,0} + \xi_1 - \xi_2$$
$$N_U = N_{U,0} \quad + \xi_2$$

from writing for each component $\quad N_i = N_{i,0} + \sum_{j=1}^{j=R} (\upsilon_i \xi_j)$

For constant volume

$$C_A = C_{A,0} - \xi'_1$$
$$C_D = C_{D,0} + \xi'_1 - \xi'_2 \quad \text{where} \quad \xi'_i = \xi_i / V$$
$$C_U = C_{U,0} \quad\quad + \xi'_2$$

Component A is unique to equation 1 and U is unique to 2. For any system, a set of ISE can always be found such that each has a component unique to that equation. Write component balances for those "unique components" to save algebra in order to end up with an ODE for each extent.

$$-\frac{dC_A}{dt} = \frac{d\xi'_1}{dt} = (k_1 + k_3)(C_{A,0} - \xi'_1)$$
$$\frac{dC_U}{dt} = \frac{d\xi'_2}{dt} = k_2(C_{D,0} + \xi'_1 - \xi'_2) + k_3(C_{A,0} - \xi'_1)$$

Now we can integrate these two equations to get ξ'_1 and ξ'_2 at any time, then use the stoichiometric table to get concentrations of all three components.

The advantage of this option over that of writing a balance for each component is that errors in conservation of elements are eliminated when numerically integrating the ODEs.

Simulations in ReactorLab

See Division 5 Multiple Reactions in ReactorLab. Get ReactorLab at `http://www.ReactorLab.net`

Lab 1 Stoichiometry discusses the minimum number of component balances that must be integrated in a reactor with multiple reactions.

Lab 2 Ethylene Oxidation has a simulation of an ethylene oxidation reactor with a series-parallel reaction system.

Lab 3 Parallel Reactions has a simulation of parallel reaction cases 1 and 2 above.

Lab 4 Series Reactions has a simulation of the series reaction case above.

Additional resources

Schmidt's book - on library reserve & online via `http://roger.ucsd.edu/record=b7179459~S9`
    Chapter 4

Levenspiel's book - on library reserve
    Chapters 7 & 8

Fogler's *Essentials* book - on library reserve
    Chapter 8

Also see Fogler's web resources >> `http://www.umich.edu/~essen/html/08chap/frames.htm`