A First Course on Kinetics and Reaction Engineering
Supplemental Unit S1. Identifying Independent Reactions

Defining the Problem

Given a group of chemical reactions, find a complete mathematically independent sub-set of those reactions where every reaction in the original group can be written as a linear combination of the reactions in the complete mathematically independent sub-set. In order to solve this kind of problem numerically, you will need software that can find the rank of a matrix.

Information and Data Required for Numerical Solution

Input required when identifying independent reactions numerically:

- A reaction matrix constructed from the stoichiometric coefficients of the species that participate in the group of reactions taking place; each column is associated with one of the chemical species, and each row is associated with one of the reactions
- Code or a script to sequentially process the rows of the matrix above (or you can do so manually) as follows, starting with an empty test matrix
  - temporarily add the next row of the reaction matrix to the test matrix and find its rank
    - if the number of rows in the resulting test matrix equals its rank, retain the added row in the test matrix
    - if the number of rows in the resulting test matrix is greater than its rank, remove the added row from the test matrix

After all the rows in the reaction matrix have been processed, the reactions in the final test matrix represent a complete mathematically independent sub-set of the original reactions.

Overview of the Numerical Method

I don't know of mathematics software packages with pre-programed functions for finding a complete mathematically independent sub-set of reactions, but most do include a function for finding the rank of a matrix. The rank of a matrix is equal to the number of mathematically independent rows in the matrix. As noted above, you will need to write a script or manually implement the process described in the second bullet item. In each iteration of that process it is necessary to find the rank of a matrix, and that can be done numerically using many different brands of mathematics software. (For those who wish to use MATLAB mathematics software, the next section presents a script that automates the process described above in the second bullet item.)

There are a few ways to find the rank of a matrix, and different brands of mathematics software may utilize different methods. Gaussian elimination[1] is one such method, and it will be described here.

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[1] This example assumes some familiarity with matrix operations in reducing the matrix to zeroes below the diagonal. A more complete description of allowable matrix manipulations can be found, for example, in N. R. Amundson, "Mathematical Methods in Chemical Engineering, Matrices and Their Application." Prentice-Hall, Englewood Cliffs, NJ, 1966.

For small matrices it is easy to perform Gaussian elimination by hand, but there are many opportunities for making arithmetic mistakes when you do so. In order to describe the Gaussian elimination process, let $c_{i,j}$ represent the current value of the matrix element in row i and column j. The process for Gaussian elimination is then as follows:

- Begin by processing the first column as follows
  - If $c_{1,1}$ is equal to zero, find a row with a non-zero entry in column 1 and switch those two rows (after this step, $c_{1,1}$ will be non-zero)
  - For each row, n, below row 1 with a non-zero entry in column 1
    - Multiply through row n by ($-c_{1,1}/c_{n,1}$)
    - Add the resulting row, column by column, to row 1
    - Replace row n with the result (row n will now have a zero in column 1)
  - If any rows contain only zeros, delete those rows from the matrix (these rows are a linear combination of the rows above them)
- Process the second column as follows
  - If $c_{2,2}$ is equal to zero, find a row below it with a non-zero entry in column 2 and switch those two rows (after this step, $c_{2,2}$ will be non-zero)
  - For each row, n, below row 2 with a non-zero entry in column 2
    - Multiply through row n by ($-c_{2,2}/c_{n,2}$)
    - Add the resulting row, column by column, to row 2
    - Replace row n with the result (row n will now have a zero in column 2)
  - If any rows contain only zeros, delete those rows from the matrix (these rows are a linear combination of the rows above them)
- Repeat the same process for the third, fourth, etc. columns until no rows remain
- The number of rows in the final matrix is the rank of the original matrix

MATLAB Script File

MATLAB contains a function named `rank` that computes the rank of a matrix. In order to simplify the process of identifying independent reactions, and to allow you to focus on kinetics and reaction engineering instead of computer programming, a MATLAB script file named IndEqns.m is provided with this supplemental unit. Given a matrix named `C` that has been constructed according to the first bullet point for input requirements, the MATLAB script file IndEqns.m determines the corresponding number of mathematically independent reactions and it generates a complete mathematically independent subset of the reactions. The script requires no modification prior to its use. It only needs to be located in the MATLAB search path. It does require the matrix to be named `C` and to be present in the MATLAB workspace. The use of this script is illustrated in the example that accompanies this supplemental unit.