A First Course on Kinetics and Reaction Engineering
Example S1.1

This example shows how to identify a complete mathematically independent set of chemical reactions using the MATLAB script file IndEqns.m that accompanies Supplemental Unit S1. This example is taken from the solution to Example 1.4 from Unit 1. In that example, reactions (1) through (6) were taking place, and it was necessary to find a mathematically independent sub-set of those reactions.

$$CO + 2\ H_2 \rightleftarrows CH_3OH \quad (1)$$

$$CO_2 + 3\ H_2 \rightleftarrows CH_3OH + H_2O \quad (2)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (3)$$

$$CO + 3\ H_2 \rightleftarrows CH_4 + H_2O \quad (4)$$

$$CO_2 + 4\ H_2 \rightleftarrows CH_4 + 2\ H_2O \quad (5)$$

$$CH_4 + H_2O \rightleftarrows CH_3OH + H_2 \quad (6)$$

Solution

As described in the informational reading, in order to identify a sub-set of mathematically independent reactions you need mathematics software that will determine the rank of a matrix and you need to provide the following:

- 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 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, return the final test matrix

Here, the MATLAB script file, IndEqns.m, will be used to provide the code described in the second bullet above, so all that is necessary is to generate the reaction matrix and then execute the script file. The reaction matrix will be represented as $\underline{\underline{C}}$. Let the columns of $\underline{\underline{C}}$, in order from left to right, correspond to CO, H_2, CH_3OH, CO_2, H_2O and CH_4. Let the rows of $\underline{\underline{C}}$, in order from top to bottom, correspond to reactions (1) through (6). The reaction matrix, $\underline{\underline{C}}$, can then be constructed so that the entry at row j and

column i is the stoichiometric coefficient ($\nu_{i,j}$) of the corresponding species in the corresponding reaction. The result is given in equation (7).

$$\underline{\underline{C}} = \begin{bmatrix} -1 & -2 & 1 & 0 & 0 & 0 \\ 0 & -3 & 1 & -1 & 1 & 0 \\ -1 & 1 & 0 & 1 & -1 & 0 \\ -1 & -3 & 0 & 0 & 1 & 1 \\ 0 & -4 & 0 & -1 & 2 & 1 \\ 0 & 1 & 1 & 0 & -1 & -1 \end{bmatrix} \tag{7}$$

The matrix $\underline{\underline{C}}$ was entered into the MATLAB workspace, and it was given the name C, as shown in Listing 1. Note that that the matrix must be named C because that name is assumed by the script file. Once that was done, all that was necessary was to type “IndEqns” at the MATLAB command prompt (the file IndEqns.m must be in the MATLAB search path). The results of running the MATLAB script are shown in Listing 2. The resulting independent reactions matrix contains three rows, so there are three reactions in the independent sub-set. Recalling that the columns in that matrix correspond, in order from left to right, to CO, H_2, CH_3OH, CO_2, H_2O and CH_4, you can see that the independent sub-set includes reactions (1), (2), and (4).

```
C =

   -1   -2    1    0    0    0
    0   -3    1   -1    1    0
   -1    1    0    1   -1    0
   -1   -3    0    0    1    1
    0   -4    0   -1    2    1
    0    1    1    0   -1   -1
```

Listing 1.

```
IndEqns

n_ind =
    3

IndEqs =
   -1   -2    1    0    0    0
    0   -3    1   -1    1    0
   -1   -3    0    0    1    1
```

Listing 2.