

A First Course on Kinetics and Reaction Engineering

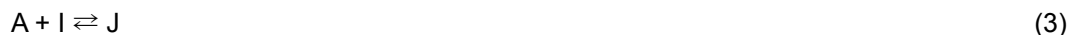
Example 6.1

Problem Purpose

This problem shows how to check the plausibility of a mechanism, determine whether it is an open or closed sequence of reaction steps and use it to generate a rate expression for the macroscopically observed, non-elementary reaction to which it corresponds. *It also expands upon the information presented in the informational reading with respect to steps that are unimolecular in either the forward or reverse direction.*

Problem Statement

When the chemical species A reacts, analysis of the composition of the system over time suggests that reaction (1) is taking place. However careful research using a number of spectroscopic techniques indicates that in fact, reactions (2) through (4) are actually taking place at the molecular level, not reaction (1). Do reactions (2) through (4) represent a plausible mechanism for reaction (1)? If so, does the mechanism consist of an open sequence or steps or a closed sequence of steps, and what is the rate of reaction (1) with respect to A?



Problem Analysis

To check the plausibility of a mechanism, one needs to determine whether it obeys the three rules given in the information reading. If it is plausible, then one can determine whether it is a closed sequence of steps by identifying propagation steps. If it contains propagation steps, it is a closed sequence of steps, otherwise it is an open sequence. The rate with respect to a reactant or product is simply the sum of the rate of each step with respect to that species.

Problem Solution

In order to be a plausible mechanism, there must be a linear combination of the steps that is equivalent to macroscopically observed, non-elementary reaction, the steps must be elementary (and therefore reversible) and it must be consistent with all available experimental data, not just kinetics studies. The problem statement says that the mechanism was proposed on the basis of careful spectroscopy experiments, so we can assume that it is consistent with all available data. The three mechanistic steps are each indicated as reversible reactions by the use of double arrows, but they are not elementary. Specifically, reaction (2) is unimolecular in both directions while reactions (3) and (4) are each

unimolecular in one direction. Example 5.3 points out that an elementary reaction cannot be unimolecular, and it notes that there are additional theories that apply to unimolecular reactions. In most cases, however, a unimolecular reaction will obey the rate expression predicted by transition state theory, except at very low pressures (this will be demonstrated in Unit 7). Therefore, *for the purpose of generating a rate expression from the mechanism, we can allow unimolecular reactions as mechanistic steps*. This practice will be followed in the remainder of this course, but one should always bear in mind that including a unimolecular reaction in a reaction mechanism introduces an assumption and results in some simplification of the rate expression generated from the mechanism. In a rigorous study, the theory of unimolecular reactions should be applied to such steps.

It remains to determine whether there is a linear combination of the mechanistic steps that is equal to the macroscopically observed, non-elementary reaction. If this is true, then the macroscopically observed, non-elementary reaction is not mathematically independent from the set of reactions comprising the mechanism. Basically, the way to do this is first to determine the number of mathematically independent reactions in the mechanism. Then the macroscopically observed, non-elementary reaction is added in and the number of mathematically independent reactions is determined again. If adding the macroscopically observed, non-elementary reaction does not increase the number of mathematically independent reactions, then the macroscopically observed, non-elementary reaction is a linear combination of the reactions comprising the mechanism. As described in Supplemental Unit S1, a set of chemical reactions can be checked to determine whether they are mathematically independent manually or using software that can determine the rank of a matrix. In either case you will need to do the following:

- create a reaction matrix containing the stoichiometric coefficients, where each column corresponds to one species and each row corresponds to one reaction.
- process the matrix as follows:
 - step 1: determine its rank
 - ▶ if the rank equals the number of reactions, the reactions are mathematically independent and you are done
 - ▶ otherwise proceed to the step 2
 - step 2: remove one row from the matrix and determine the rank of the resulting matrix
 - ▶ if the rank remains the same, the reaction corresponding to the removed equation was a linear combination of the remaining reactions, so leave it out of the matrix
 - ▶ If the rank decreases by one, the removed row corresponds to a mathematically independent reaction, so put it back into the matrix
 - step 3: if the rank now equals the number of rows remaining in the matrix, the corresponding reactions are mathematically independent and you are done, otherwise repeat step 2 removing a different row

Here, the reaction matrix will be represented as \underline{C} . The columns of \underline{C} , in order from left to right will correspond, to the species A, B, I and J. Rows of the first version of \underline{C} , in order from top to bottom, will correspond to reactions (2) through (4). The first reaction matrix, \underline{C} , can then be constructed so that the

entry at row j and column i is the stoichiometric coefficient (v_{ij}) of the corresponding species in the corresponding reaction. The result is given in equation (5), and using this matrix reveals that there are 3 mathematically independent reactions in the mechanism.

$$\underline{\underline{C}} = \begin{bmatrix} -1 & 0 & 1 & 0 \\ -1 & 0 & -1 & 1 \\ 1 & 1 & 0 & -1 \end{bmatrix} \quad (5)$$

The second reaction matrix is created by adding a row that corresponds to reaction (1). If that row is added at the bottom of the $\underline{\underline{C}}$ matrix shown in equation (5), equation (6) results, and using this matrix reveals that it, too, contains 3 mathematically independent reactions. Thus, the macroscopically observed, non-elementary reaction is a linear combination of the steps in the mechanism. Since the mechanism consisting of reactions (2) through (4) satisfies the three rules given previously, it is plausible as the mechanism for reaction (1).

$$\underline{\underline{C}} = \begin{bmatrix} -1 & 0 & 1 & 0 \\ -1 & 0 & -1 & 1 \\ 1 & 1 & 0 & -1 \\ -1 & 1 & 0 & 0 \end{bmatrix} \quad (6)$$

The problem next asks whether the steps in the mechanism form a closed sequence or not. Looking at the mechanism, we see two species that appear in the mechanism that do not appear in the macroscopically observed, non-elementary reaction, namely I and J. These species are therefore reactive intermediates. A closed sequence of steps would include two propagation steps where one step consumes I and generates J, where the other step consumes J and generates I and where the sum of the two steps equals the macroscopically observed, non-elementary reaction. Reaction (3) consumes I and generates J, but there is no corresponding step that consumes J and generates I. Therefore, this mechanism involves an open sequence.

Finally, the problem asks for a rate expression for the rate of reaction (1) with respect to A. The rate with respect to a reactant or product is simply the sum of the rate of each step with respect to that species. In this case, the rate of reaction (1) with respect to A is equal to the sum of the rates of reactions (2) through (4) with respect to A, as expressed in equation (7). Since each of the mechanistic steps is elementary (noting the warning above about the unimolecular steps), their rate expressions are given by equation (8). Substituting equation (8) into equation (7) gives equation (9), and expanding the summation leads to the desired rate expression, equation (10).

$$r_{A,1} = \sum_{s=2}^4 v_{A,s} r_s \quad (7)$$

$$r_{i,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} \nu_{i,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{\nu_{n,s}} \right) \quad (8)$$

$$r_{A,1} = \sum_{s=2}^4 \nu_{A,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{\nu_{n,s}} \right) \quad (9)$$

$$r_{A,1} = -k_{2,f} [A] + k_{2,r} [I] - k_{3,f} [A][I] + k_{3,r} [J] + k_{4,f} [J] - k_{4,r} [A][B] \quad (10)$$

Calculation Details Using MATLAB

A MATLAB script file named IndEqns.m is provided with Supplemental Unit S1. That script can be used to check a reaction matrix to determine whether the corresponding reactions are mathematically independent and to identify a complete mathematically independent subset, if they are not. To do so, the script file must be located in the current MATLAB working directory or in the MATLAB search path.

Before executing IndEqns, a reaction matrix named C must be created from the set of reactions to be tested. Then, upon execution, the script will go through the process of determining rank and eliminating reactions that are not independent. Upon completion, the output will consist of a variable named n_ind that is equal to the number of mathematically independent reactions in the original set and a matrix named IndEqns that is the reaction matrix for one complete mathematically independent subset containing n_ind of the original reactions. This can be done directly at the MATLAB command prompt, but instead, I created a MATLAB function named Example_6_1; it accompanies this solution as Example_6_1.m. In that function, as shown in Listing 1, the \underline{C} matrix shown in equation (5) is defined with the variable name C, and IndEqns is executed to find the number of mathematically independent reactions. The variable C is then redefined to be the \underline{C} matrix shown in equation (6), and IndEqns is executed again to find the number of mathematically independent reactions. The resulting output is shown in Listing 2; it indicates that there are 3 mathematically independent reactions in both versions of the \underline{C} matrix.

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```
% MATLAB file used in the solution of Example 6.1 of A First Course on
% Kinetics and Reaction Engineering.
%
function z = Example_6_1
    % Reaction matrix containing the mechanistic steps
    C = [-1 0 1 0
         -1 0 -1 1
          1 1 0 -1]
    IndEqns
    % Reaction matrix adding the macroscopically observed overall
    % reaction
    C = [C; -1 1 0 0]
    IndEqns
end % of Example_6_1.m
```

Listing 1. MATLAB function used in the solution of this problem.

```
>> Example_6_1

C =

    -1     0     1     0
    -1     0    -1     1
     1     1     0    -1

n_ind =

     3

IndEqns =

    -1     0     1     0
    -1     0    -1     1
     1     1     0    -1

C =

    -1     0     1     0
    -1     0    -1     1
     1     1     0    -1
    -1     1     0     0

n_ind =

     3

IndEqns =

    -1     0     1     0
    -1     0    -1     1
     1     1     0    -1
```

Listing 2. Output from execution of the MATLAB function Example_6_1