A First Course on Kinetics and Reaction Engineering

Class 6 on Unit 6

Where We've Been

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
  - A. Rate Expressions
    - 4. Reaction Rates and Temperature Effects
    - 5. Empirical and Theoretical Rate Expressions
    - 6. Reaction Mechanisms
    - 7. The Steady State Approximation
    - 8. Rate Determining Step
    - 9. Homogeneous and Enzymatic Catalysis
    - 10. Heterogeneous Catalysis
  - B. Kinetics Experiments
  - C. Analysis of Kinetics Data
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors

Non-Elementary Reactions

- What appears to be happening when observed macroscopically is actually the net effect of two or more elementary reactions occurring at the molecular level
    - Collectively the set of elementary reactions that actually occur at the molecular level is called the reaction mechanism
- Mechanism rules
    - Each step must be an elementary reaction, and therefore must be reversible
    - Must be consistent with all available experimental data, not just kinetics data
    - There must be some linear combination of the mechanistic steps that exactly equals the macroscopically observed, non-elementary reaction
- Species that appear in the reaction mechanism, but not in the macroscopically observed, non-elementary reaction, are called reactive intermediates
- The rate of consumption of a reactant, *i*, in the apparent macroscopic reaction, *j*, is the sum of the rate of consumption of that reactant in each of the mechanistic steps, *s*

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

Chain Reaction (Closed Sequence) Mechanisms

- Must contain inititation/termination steps
  - Initiation Step - generates one or more reactive intermediates without consuming any
  - Termination Step - consumes one or more reactive intermediates without generating any
- Must contain propagation steps
  - Propagation Steps
    - Each propagation step consumes one reactive intermediate and generate another one
    - There is a linear combination of the propagation steps that equals the macroscopically observed, non-elementary reaction
      - For this reason, the steps are said to form a closed sequence
- May contain other kinds of steps
  - Transfer Step - stops one growing chain and starts another
    - Polymerization is a typical example
  - Branching - consumes one reactive intermediate and generates two more
    - In exothermic systems, this can lead to explosions
- Mechanisms that do not have propagation steps will consist of an open sequence of steps
  - Every step in an open sequence mechanism must occur at least once each time the non-elementary reaction occurs
  - The stoichiometric number of a step is the number of time it must occur for each occurrence of the non-elementary reaction

Questions?

Testing the Plausibility of a Mechanism

The non-elementary, macroscopically observed reaction (1) has been studied using a variety of techniques. The experimental results are consistent with the mechanism presented in reactions (2) through (4), each of which is reversible.

$$A + 2\,B \rightleftarrows Y + Z \qquad (1)$$

$$A + B \rightleftarrows J + K \qquad (2)$$

$$B + J \rightleftarrows Y + Z \qquad (3)$$

$$Z + K \rightleftarrows A + Y \qquad (4)$$

Is there a linear combination of the mechanistic steps that sums to give the macroscopically observed reaction?

First try to answer this question without determining the number of mathematically independent equations, that is, by inspection.

With more complicated mechanisms, obtaining an answer will require the determination of the number of mathematically independent equations; set up the reaction matrices needed in order to do this.

Testing the Plausibility of a Mechanism

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Is there a linear combination of the mechanistic steps that sums to give the macroscopically observed reaction?

- It can be seen by inspection that reaction (1) cannot be generated by any linear combination of reactions (2) through (4).
- There are a few ways to see this, one is to note that
  - Reaction (2) is the only step that consumes an A, as required by the overall (macroscopically observed) reaction (1)
  - Reaction (2) generated the reactive intermediate K
  - The only step that will consume the reactive intermediate K, will re-generate the reactant A

Testing the Plausibility of a Mechanism

$A + 2B \rightleftarrows Y + Z \qquad (1)$

$A + B \rightleftarrows J + K \qquad (2)$

$B + J \rightleftarrows Y + Z \qquad (3)$

$Z + K \rightleftarrows A + Y \qquad (4)$

- If reaction (1) ***is not*** mathematically independent with respect to reactions (2) through (4) then there is a linear combination of reactions (2) through (4) that is equal to reaction (1)
  - If this is true, the number of mathematically independent equations from among reactions (2) through (4) will equal the number of mathematically independent equations from among reactions (1) through (4)
  - If this is true, the two reaction matrices below will have the same rank
    - Columns, from left to right correspond to A, B, Y, Z, J and K

$$\underline{\underline{C}} = \begin{bmatrix} -1 & -1 & 0 & 0 & 1 & 1 \\ 0 & -1 & 1 & 1 & -1 & 0 \\ 1 & 0 & 1 & -1 & 0 & -1 \end{bmatrix}$$

$$\underline{\underline{C}} = \begin{bmatrix} -1 & -1 & 0 & 0 & 1 & 1 \\ 0 & -1 & 1 & 1 & -1 & 0 \\ 1 & 0 & 1 & -1 & 0 & -1 \\ -1 & -2 & 1 & 1 & 0 & 0 \end{bmatrix}$$

Using MATLAB and IndEqns

$$\underline{\underline{C}} = \begin{bmatrix} -1 & -1 & 0 & 0 & 1 & 1 \\ 0 & -1 & 1 & 1 & -1 & 0 \\ 1 & 0 & 1 & -1 & 0 & -1 \end{bmatrix}$$

$$\underline{\underline{C}} = \begin{bmatrix} -1 & -1 & 0 & 0 & 1 & 1 \\ 0 & -1 & 1 & 1 & -1 & 0 \\ 1 & 0 & 1 & -1 & 0 & -1 \\ -1 & -2 & 1 & 1 & 0 & 0 \end{bmatrix}$$

```
% MATLAB file used in the solution of Activity 6.1 of A First Course on
% Kinetics and Reaction Engineering.
%
function z = Activity_6_1
   % Reaction matrix containing the mechanistic steps
   C = [-1 -1 0 0 1 1
      0 -1 1 1 -1 0
      1 0 1 -1 0 -1]
   IndEqns
   % Reaction matrix adding the macroscopically observed overall reaction
   C = [C; -1 -2 1 1 0 0]
   IndEqns
end % of Activity_6_1.m
```

```
>> Activity_6_1

C =

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

n_ind =

     3

IndEqs =

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

C =

    -1    -1     0     0     1     1
     0    -1     1     1    -1     0
     1     0     1    -1     0    -1
    -1    -2     1     1     0     0

n_ind =

     4

IndEqs =

    -1    -1     0     0     1     1
     0    -1     1     1    -1     0
     1     0     1    -1     0    -1
    -1    -2     1     1     0     0
```

Two Mechanisms

Macroscopically Observed Reaction

$2\ N_2O_5 \rightleftarrows 2\ N_2O_4 + O_2$

$H_2 + D_2 \rightleftarrows 2\ HD$

Mechanism

$N_2O_5 \rightleftarrows NO_2 + NO_3$

$NO_2 + NO_3 \rightleftarrows NO_2 + O_2 + NO$

$NO + N_2O_5 \rightleftarrows 3\ NO_2$

$2\ NO_2 \rightleftarrows N_2O_4$

$2\ H_2 \rightleftarrows H_3^+ + H^-$

$H_3^+ + D_2 \rightleftarrows H_2 + HD_2^+$

$HD_2^+ + D_2 \rightleftarrows HD + D_3^+$

$D_3^+ + H_2 \rightleftarrows D_2 + H_2D^+$

$H_2D^+ + H_2 \rightleftarrows HD + H_3^+$

- For each of the two mechanisms given above
  - Identify all reactive intermediates
  - Determine whether the mechanism is an open sequence of steps or a closed sequence of steps (chain mechanism)
  - Write an expression for the rate of the apparent, macroscopically observed reaction with respect to one of the reactants or products in that reaction

Two Mechanisms

Macroscopically Observed Reaction

$2\ N_2O_5 \rightleftarrows 2\ N_2O_4 + O_2$	(1)	$H_2 + D_2 \rightleftarrows 2\ HD$

Mechanism

$N_2O_5 \rightleftarrows NO_2 + NO_3$	(2)	$2\ H_2 \rightleftarrows H_3^+ + H^-$
$NO_2 + NO_3 \rightleftarrows NO_2 + O_2 + NO$	(3)	$H_3^+ + D_2 \rightleftarrows H_2 + HD_2^+$
$NO + N_2O_5 \rightleftarrows 3\ NO_2$	(4)	$HD_2^+ + D_2 \rightleftarrows HD + D_3^+$
$2\ NO_2 \rightleftarrows N_2O_4$	(5)	$D_3^+ + H_2 \rightleftarrows D_2 + H_2D^+$
	(6)	$H_2D^+ + H_2 \rightleftarrows HD + H_3^+$

Reactive Intermediates

NO_2, NO_3, NO	H_3^+, H^-, HD_2^+, H_2D^+, D_3^+

Open or closed?

open (no propagation steps)	closed (steps 3 through 6)

Rate Expression

$$r_{O_2,1} = k_{3,f}\left[NO_2\right]\left[NO_3\right] - k_{3,r}\left[NO_2\right]\left[O_2\right]\left[NO\right]$$

$$r_{HD,1} = k_{4,f}\left[HD_2^+\right]\left[D_2\right] - k_{4,r}\left[HD\right]\left[D_3^+\right] + k_{6,f}\left[H_2D^+\right]\left[H_2\right] - k_{6,r}\left[HD\right]\left[H_3^+\right]$$

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