A First Course on Kinetics and Reaction Engineering

Class 4 on Unit 4

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**

Unit 4 Summary

- **Rates**
  - Rate with respect to a participant species: $r_{i,j} = \dfrac{1}{V} \dfrac{dn_{i,j}}{dt}$
  - Generalized rate: $r_j = \dfrac{1}{V_{fluid}} \dfrac{d\xi_j}{dt}$
  - Cell growth rate: $r_g = \dfrac{1}{V} \dfrac{dm_{cells}}{dt}$
  - Specific cell growth rate: $\mu = \dfrac{r_g}{C_{cells}}$
  - Relationships
    - $r_{i,j} = \nu_{i,j} r_j$ $\quad \dfrac{r_{i,j}}{\nu_{i,j}} = \dfrac{r_{k,j}}{\nu_{k,j}}$

- **Normalization of Rates**
  - Makes the rate an intensive quantity
  - Best to normalize using the size of the location where the reaction actually occurs
    - fluid volume, catalyst area, interfacial area between two fluids, etc.

- **Rate Expressions**
  - Mathematical model for net rate as a function of temperature, pressure and composition
  - Single valued
  - Must evaluate to zero at equilibrium values of temperature, pressure and composition

- Source of rate expressions
  - Not from stoichiometry (except special cases to be discussed in Units 5 and 6)
  - Determined experimentally
    - Choose a reactor for the experiments
      - Generate design equations for that reactor and validate them
    - Gather experimental data that, at the minimum, span the range of the environmental variables for which the rate expression will be used
    - Pick a mathematical function to be tested as a rate expression
    - Substitute the rate expression into the design equations and fit the resulting equation(s) to the experimental data
    - Decide whether the fit of the design equation to the data is acceptable; pick new mathematical function and iterate if it is not acceptable
- Temperature dependent quantities in rate expressions
  - Concentrations or partial pressures of gasses (e. g. ideal gas law)
  - Equilibrium constants (recall from Unit 3)
  - Rate coefficients
    - Arrhenius expression is the most common model: $k_j = k_{0,j} \exp\left(\dfrac{-E_j}{RT}\right)$
      - Pre-exponential factor, $k_{0,i}$, and activation energy, E_j, commonly found by fitting the linearized Arrhenius expression to experimentally determined values of k_j at several temperatures
        - $\ln\left(k_j(T)\right) = \dfrac{-E_j}{R}\left(\dfrac{1}{T}\right) + \ln\left(k_{0,j}\right)$
    - Models other than the Arrhenius expression are sometimes used

Questions?

Effect of Stoichiometry on Reaction Rates and Extents

- You will be assigned to complete one of the three handouts for today's class and given 5 minutes to do so
- All those working on handout A will come to a consensus on the correct answers and write them on the chalkboard; those working on handout B or handout C will do the same

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- All three groups were working on the same problem; the only difference is the set of stoichiometric coefficients used when writing the reaction

- Compare the results
  - ‣ Which are the same?
  - ‣ Which are different?
    - If each group had solved a kinetics problem to find the conversion after some amount of time using one of the rate expressions that differ, would the groups get the same answer or different answers?
    - If you started solving a kinetics problem by writing a mole table based on the A handout and then used a generalized rate expression from the B handout, would you get the same answer as someone who used the A handout for both the mole table and the rate expression? Would someone who used the A handout for both the mole table and the rate expression get a different answer than someone who used the B handout for both the mole table and the rate expression?

Arrhenius Problem Types

You have been assigned to a group of three students, and your group has been assigned one of the following problems. Set up the solution to the problem you have been assigned.

1. The rate coefficient for a reaction is 0.304 min^{-1} at 30 °C. The activation energy for that rate coefficient is 61.1 kJ mol^{-1}. Assuming Arrhenius behavior, what is the rate coefficient at 65 °C?

2. If a rate coefficient doubles when the temperature is raised from 22 °C to 45 °C, what is the value of the corresponding activation energy? If the rate coefficient at 40 °C is 3.07 x 10^{-4} s^{-1}, what is its value at 32 °C?

3. The rate coefficient for a particular reaction varies with temperature as follows:

T(°C)	25	35	45	55	65
10^3 x k, min^{-1}	0.8	3.8	15.1	46.7	151

Determine the pre-exponential factor and the activation energy.

Teach Each Other

You are now the only person in your group of three who solved your problem. Each person explain to the other two how to solve your problem.

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