Lecture 3

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 3 – Thursday 1/17/2013

- Review of Lectures 1 and 2
- Building Block 1
 - Mole Balances (Review)
 - Size CSTRs and PFRs given $-r_A = f(X)$
 - Conversion for Reactors in Series
- Building Block 2
 - Rate Laws
 - Reaction Orders
 - Arrhenius Equation
 - Activation Energy
 - Effect of Temperature

Reactor Mole Balances Summary

The GMBE applied to the four major reactor types (and the general reaction $A \rightarrow B$)



$a A + b B \longrightarrow c C + d D$

Choose limiting reactant A as basis of calculation



$$X = \frac{\text{moles A reacted}}{\text{moles A fed}}$$

Reactor Mole Balances Summary In terms of Conversion



Levenspiel Plots









Building Block 2: Rate Laws Power Law Model:

$$-r_A = kC_A^{\alpha}C_B^{\beta}$$

 α order in A β order in B Overall Rection Order = $\alpha + \beta$

Building Block 2: Rate Laws $2A+B \rightarrow 3C$

A reactor follows an elementary rate law if the reaction orders just happens to agree with the stoichiometric coefficients for the reaction as written. e.g. If the above reaction follows an elementary rate law $-r_{A} = k_{A}C_{A}^{2}C_{B}$

2nd order in A, 1st order in B, overall third order

Building Block 2: Rate Laws

Rate Laws are found from Experiments
 2A+B→3C

WCI KUMOL

- Rate Laws could be non-elementary. For example, reaction could be:
 - Second Order in A
 - Zero Order in B
 - > Overall Second Order

$$-r_A = k_A C_A^2$$
$$-r_B = k_B C_A^2$$
$$r_C = k_C C_A^2$$

Relative Rates of Reaction

 $aA + bB \rightarrow cC + dD$

$$A + \frac{b}{a}B \to \frac{c}{a}C + \frac{d}{a}D$$

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Relative Rates of Reaction $2A + B \rightarrow 3C$

Given
$$-r_A = 10 \frac{mol}{dm^3 \cdot s}$$

Then
$$\frac{r_A}{-2} = \frac{r_B}{-1} = \frac{r_C}{3}$$

$$-r_{\mathbf{B}} = \frac{-r_{A}}{2} = 5 \frac{mol}{dm^{3} \cdot s}$$

$$r_C = \frac{-3}{2}r_A = 15\frac{mol}{dm^3 \cdot s}$$

Reversible Elementary Reaction

A+2B
$$\stackrel{k_{A}}{\leftarrow} 3C$$

$$-r_{A} = k_{A}C_{A}^{2}C_{B} - k_{-A}C_{C}^{3} = k_{A}\left[C_{A}^{2}C_{B} - \frac{C_{C}^{3}}{k_{A}/k_{-A}}\right]$$

$$=k_{A}\left[C_{A}^{2}C_{B}-\frac{C_{C}^{3}}{K_{e}}\right]$$

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Reversible Elementary Reaction

A+2B $\stackrel{k_{A}}{\leftarrow}$ 3C



$$[-r_A] = \frac{moles}{dm^3 s}$$
 $C_A = \frac{moles}{dm^3}$

$$[k] = \left[\frac{-r_A}{C_A C_B^2}\right] = \frac{mole/dm^3/s}{\left(mole/dm^3\right)\left(mole/dm^3\right)^2} = \frac{dm^6}{mole^2s}$$

A. First-Order Rate Laws





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Algorithm

How to find
$$-r_A = f(X)$$

Step 1: Rate Law $-r_A = g(C_i)$

Step 2: Stoichiometry
$$(C_i) = h(X)$$

Step 3: Combine to get $-r_A = f(X)$

Arrhenius Equation

k is the specific reaction rate (constant) and is given by the Arrhenius Equation.

where:

$$k = Ae^{-E/RT}$$



Arrhenius Equation

where:

E = Activation energy (cal/mol)

R = Gas constant (cal/mol*K)

T = Temperature (K)

A = Frequency factor (same units as rate constant k) (units of A, and k, depend on overall reaction order)



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Reaction Coordinate

The activation energy can be thought of as a barrier to the reaction. One way to view the barrier to a reaction is through the reaction coordinates. These coordinates denote the energy of the system as a function of progress along the reaction path. For the reaction:

 $A + BC \Leftrightarrow A ::: B ::: C \to AB + C$

The reaction coordinate is:





Figure 3-2 A diagram of the orbital distortions during the reaction

 $H \cdot + CH_3CH_3 \rightarrow H_2 + CH_2CH_3 \cdot$

The diagram shows only the interaction with the energy state of ethane (the C-H bond). Other molecular orbitals of the ethane also distort. [Courtesy of R. Masel, *Chemical Kinetics* (McGraw Hill, 2002), p. 594.]

Collision Theory



Why is there an Activation Energy?

We see that for the reaction to occur, the reactants must overcome an energy barrier or activation energy E_A . The energy to overcome their barrier comes from the transfer of the kinetic energy from molecular collisions to internal energy (e.g. Vibrational Energy).

- 1. The molecules need energy to disort or stretch their bonds in order to break them and thus form new bonds
- 2. As the reacting molecules come close together they must overcome both stearic and electron repulsion forces in order to react.

Distribution of Velocities

We will use the Maxwell-Boltzmann Distribution of Molecular Velocities. For a species af mass m, the Maxwell distribution of velocities (relative velocities) is:

$$f(U,T)dU = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mU^2/2k_B T} U^2 dU$$

f(U,T)dU represents the fraction of velocities between U and (U+dU).

Distribution of Velocities

A plot of the distribution function, f(U,T), is shown as a function of U:



Distribution of Velocities
Given
$$f(U,T)dU = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mU^2/2k_B T} U^2 dU$$

Let $E = \frac{1}{2}mU^2$
 $f(E,T)dE = \frac{2\pi}{(2\pi k_B T)^{3/2}} E^{1/2} e^{\frac{-E}{k_B T}} dE$

f(E,T)dE represents the fraction of collisions that have energy between E and (E+dE) f(E,T)dE=fraction of molecules with energies between E+dE

One such distribution of energies is in the following figure:



End of Lecture 3

Supplementary Material



Potentials (Morse or Lennard-Jones)

Supplementary Material

One can also view the reaction coordinate as variation of the BC distance for a fixed AC distance:



For a fixed AC distance as B moves away from C the distance of separation of B from C, r_{BC} increases as N moves closer to A. As r_{BC} increases r_{AB} decreases and the AB energy first decreases then increases as the AB molecules become close. Likewise as B moves away from A and towards C similar energy relationships are found. E.g., as B moves towards C from A, the energy first decreases due to attraction then increases due to repulsion of the AB molecules as they come closer together. We now superimpose the potentials for AB and BC to form the following figure:

Supplementary Material

