CHEMICAL REACTION ENGINEERING (SKF3223)

Chapter 5: Collection and Analysis of Rate Data

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ANALYSIS OF RATE DATA – ALGORITHM

1. Rate law

2. Mole balance – depends on reactor type

3. Write the mole balance in terms of measured variable (N_A, C_A, or P_A)
   - ☐ Batch: $-r_A$ as a function of concentrations C_A
   - ☐ Differential: $-r_A$ as a function of C_A or P_A

ANALYSIS OF RATE DATA – ALGORITHM

4. Look for simplifications:

   - ☐ Method of excess
   - ☐ Gas phase mole fraction of reactant is small, set ε = 0

5. Determine:

   - ☐ Reaction order (α, β)
   - ☐ Specific reaction rate constant, *k*
   - ☐ Activation energy, E and frequency factor, A from Arrhenius equation

BATCH REACTOR DATA

1) Differential method

CASE I $A \rightarrow products$

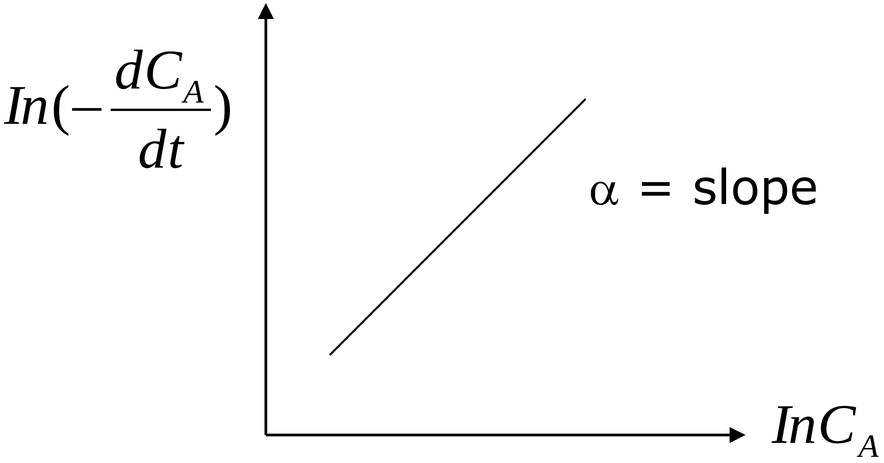
RATE LAW $-r_A = k_A C_A^{\alpha}$

MOLE BLANCE $-r_A = -\dfrac{dC_A}{dt} = k_A C_A^{\alpha}$

DETERMINE Take the natural log, ln, of both sides:

$$\ln\left(-\frac{dC_A}{dt}\right) = \alpha \ln C_A + \ln k$$

$$\mathrm{y} \quad = \mathrm{mx} \quad + \mathrm{c}$$



CASE II $A + B \rightarrow products$

RATE LAW $-r_A = k_A C_A^{\alpha} C_B^{\beta}$

To determine α and β, First, run experiment/carried out the reaction with B in excess:

$$-r_A = k' C_A^{\alpha}$$

$$k' = k C_B^{\beta} \approx k C_{B0}^{\beta}$$

Secondly, run experiment/carried out the reaction with A in excess:

$$-r_A = k'' C_B^{\beta}$$

$$k'' = k_A C_A^{\alpha} \approx k_A C_{A0}^{\alpha}$$

DETERMINE: Graphical Differentiation

- ☐ Determine the order of reaction and specific reaction rate from batch data for reaction A→B : Graphical, numerical, polynomial fit

t (min)	0	3	5	8	10	12	15	17.5
C_A (mol/dm^3)	4.0	2.89	2.25	1.45	1.0	0.65	0.25	0.07

- ☐ Rate Law

$$-r_A = -\frac{dC_A}{dt} = k_A C_A^{\alpha}$$

$$\ln\left(-\frac{dC_A}{dt}\right) = \alpha \ln C_A + \ln k$$

$$\mathrm{y} \quad = \mathrm{mx} \quad + \mathrm{c}$$

- ☐ **dC_A/dt :** is determine by calculating and plotting **- $\Delta C_A/\Delta t$ as a function of time, t**

DETERMINE: Numerical method

- Can be used when the data points in the independent variables are **equally spaced**, such as $t_1 - t_0 = t_2 - t_1 = \Delta t$

- Initial point : $$\left[\frac{dC_A}{dt}\right]_{t_0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$$

- Interior points : $$\left[\frac{dC_A}{dt}\right]_{t_i} = \frac{1}{2\Delta t}\left(C_{A(i+1)} - C_{A(i-1)}\right)$$

- Last point : $$\left[\frac{dC_A}{dt}\right]_{t_5} = \frac{1}{2\Delta t}\left(C_{A3} - 4C_{A4} + 3C_{A5}\right)$$

BATCH REACTOR DATA

1) Integral method (assume - best straight line)

$$A \rightarrow products$$

MOLE BLANCE

$$\frac{dC_A}{dt} = r_A$$

Zero order :

$$r_A = -k$$

COMBINE

$$C_A = C_{A0} - kt$$

A plot of the **C_A as a function of t** will be linear with slope *(-k)*

BATCH REACTOR DATA

1) Integral method (assume - best straight line)

First order : $-r_A = kC_A$

COMBINE

$$In\frac{C_{A0}}{C_A} = kt$$

A plot of the [In (**C_{A0}/C_A)] as a function of t** will be linear with slope *(k)*

Second order : $-r_A = kC_A^2$

COMBINE

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

A plot of the **1/C_A as a function of t** will be linear with slope *(k)*

METHOD OF INITIAL RATE

- Used when reactions are REVERSIBLE
- The reaction is assumed to have a rate law in the form so that the initial rate is given by :

$$-r_{A0} = kC_{A0}^{\alpha}$$

- In this method, several experiment have to be run with different initial concentration of A as reactant
- Taking In :

$$\ln(-r_{A0})_0 = \ln k + \alpha \ln C_{A0}$$

$$-r_{A0} = \frac{\Delta C_{A0}}{\Delta t}$$

METHOD OF HALF-LIVES

- ☐ The half-life of the reaction, $t_{1/2}$, is defined as the time it takes for the concentration of the reactant to fall to half of its value
- ☐ α and k can be determined by analyses $t_{1/2}$ of the reaction versus initial concentration

$$A \rightarrow products$$

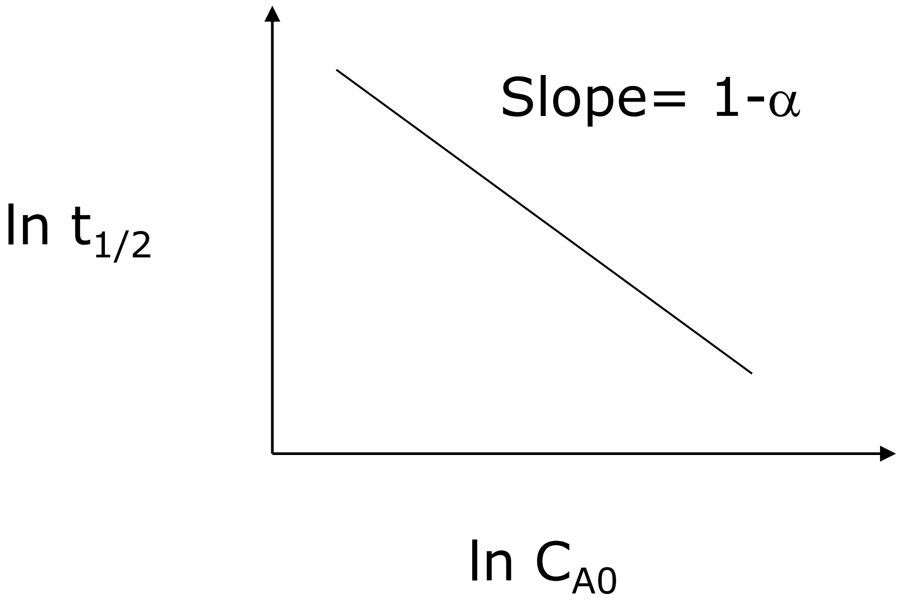
$$-\frac{dC_A}{dt} = -r_A = kC_A^{\alpha}$$

Integrate : $$t = \frac{1}{kC_A^{\alpha-1}(\alpha-1)}\left[\left(\frac{C_{A0}}{C_A}\right)^{\alpha-1} - 1\right]$$

$t = t_{1/2}$ when $C_A = ½\ C_{A0}$: $$t_{1/2} = \frac{2^{\alpha-1}-1}{k(\alpha-1)}\left(\frac{1}{C_{A0}^{\alpha-1}}\right)$$

Taking the natural log of both sides :

$$\ln t_{1/2} = \ln \frac{2^{\alpha-1}-1}{k(\alpha-1)} + (1-\alpha)\ln C_{A0}$$



REFERENCES

Main Reference:

1. Fogler,H.S., “*Elements of Chemical Reaction Engineering*”, 4th Edition,Prentice Hall, New Jersey, 2006.

Other References:

1. Davis, M.E and Davis, R.J, *“Fundamentals of Chemical Reaction Engineering”,* Mc-Graw-Hill, New York, 2003
2. Schmidt, L.D, “*The Engineering of Chemical Reactions”*, Oxford, New York, 1998
3. Levenspiel,O., “*Chemical Reaction Engineering*”, 3rd Edition, Wiley,New York, 1998
4. Smith,J., “*Chemical Engineering Kinetics*”, 3rd Edition, McGraw-Hill, New York, 1981