Reaction Engineering

Part-I(Chapter-2)-07-09-20

Kinetic Analysis in a Batch Reactor

There are two methods for batch reactor data analysis

- Differential Method of Analysis
- Integral Method of Analysis

Differential Method of Analysis

In order to explain the differential method, we may consider the elementary reaction

- $aA \rightarrow B$

If the order of reaction is assumed to be p and the kinetic equation used is

$$-r_A = -\frac{dC_A}{dt} = kC_A^p \qquad (17)$$

Differential Method of Analysis

Taking logarithm on both side of eqn. (4.17), one can obtain

$$\ln(-r_A) = ln\left(-\frac{dC_A}{dt}\right) = \ln k + p\, ln(C_A) \qquad (18)$$

In batch reactor, the reactor data is available as concentration of A (C_A) versus time (t).

The concentrations are then plotted with respect to time to obtain a curve.

The concentration gradient or derivate $-\frac{dC_A}{dt}$ at different C_A will be determined, which will be the reaction rate $(-r_A)$.

Differential Method of Analysis

- The reaction rates at different C_A are now available. Then $ln(-r_A)$ and $ln(-C_A)$ are calculated and $ln(-r_A)$ is plotted against $ln(-C_A)$, which results a straight line plot.

- The order of reaction (p) is to be calculated from the slope of the straight line plot and the reaction rate constant (k) is to determined from the intercept $\ln k$.

- **[A] Graphical Method**

- The tangents are drawn at different reaction times or different concentrations on C_A versus t curve and the slopes of tangents are determined from the graph. The slopes will be equal to $-r_A = -\dfrac{dC_A}{dt}$.
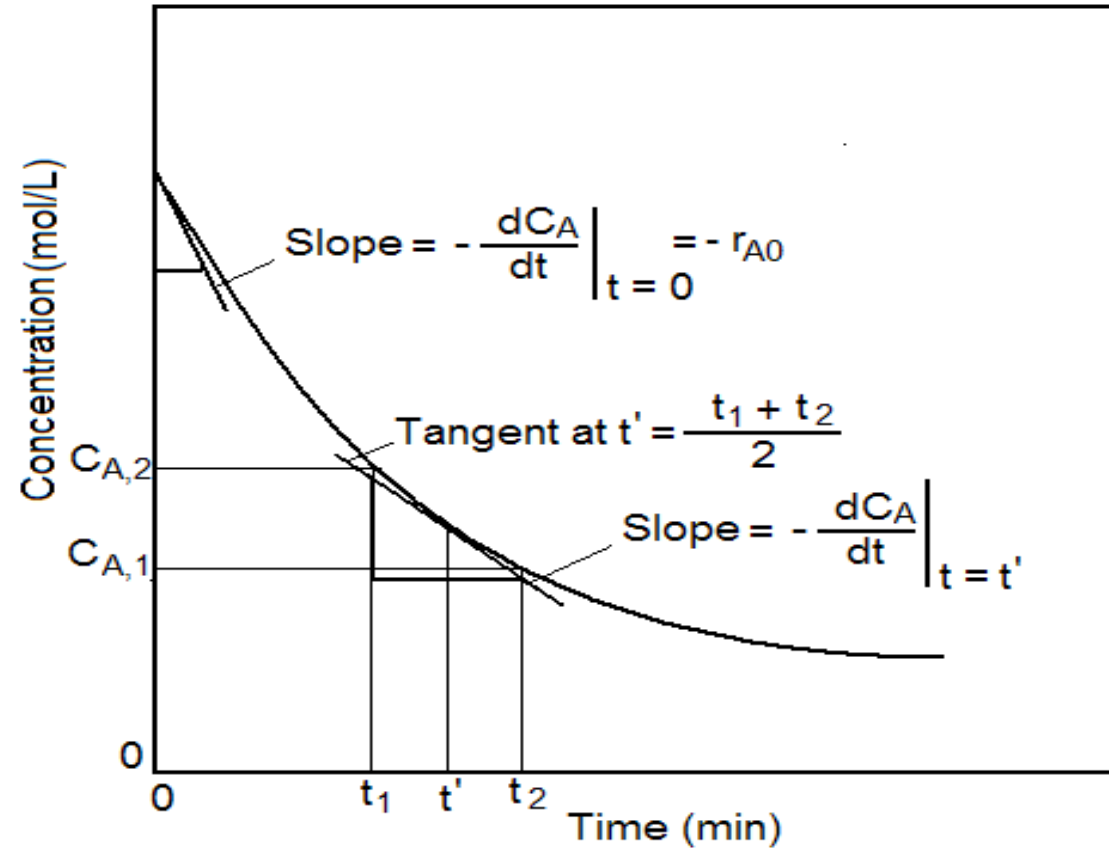
Differential Method of Analysis

For example, a point on time scale t' is chosen in such a way that $t' = (t_2 + t_1)/2$, the mean time between t_1 and t_2. The rate at $t = t'$ is the slope of the tangent drawn at t' on C_A versus t curve as represented by the equation.

- $$\frac{\Delta C_A}{\Delta t} = \frac{C_{A,1} - C_{A,2}}{t_2 - t_1} \qquad\qquad (4.19)$$

- The slopes at a different C_A are also obtained by finding the derivative from the equation

- The accuracy of the differential depends on the selection Δt, as t_2 and t_1 are approaches each other, Δt will be small.

- In general, it may be considered the concentrations at t_{n-1} and t_n are $C_{A,n-1}$ and $C_{A,n}$ respectively.

Differential Method of Analysis

The figure shows a concentration versus time curve. The y-axis is labeled "Concentration (mol/L)" and the x-axis is labeled "Time (min)".

$$\text{Slope} = -\left.\frac{dC_A}{dt}\right|_{t=0} = -r_{A0}$$

$$\text{Tangent at } t' = \frac{t_1 + t_2}{2}$$

$$\text{Slope} = -\left.\frac{dC_A}{dt}\right|_{t=t'}$$

Concentration points $C_{A,2}$ and $C_{A,1}$ are marked, with corresponding times t_1, t', t_2.

Differential method of analysis

Differential Method of Analysis

- The derivative between the points $(t_{n-1}, C_{A,n-1})$ and $(t_n, C_{A,n})$ is given by

- $$-\frac{dC_A}{dt} = \frac{-\Delta C_A}{\Delta t} = \frac{C_{A,n-1} - C_{A,n}}{t_n - t_{n-1}} \qquad (20)$$

  Where, $-\Delta C_A = C_{A,n-1} - C_{A,n}$ for the time interval $\Delta t = t_n - t_{n-1}$.

- A simplified method

- If two rates are available at two different concentrations. Let $-r_{A1}$ and $-r_{A2}$ are reaction rates for the concentrations C_{A1} and C_{A2} respectively at a fixed time 't'. Then from eq.(18),

- $\ln(-r_{A1}) = \ln k + p\, ln(C_{A1})$

- $\ln(-r_{A2}) = \ln k + p\, ln(C_{A2})$

- The order (p) and rate constant (k) are determined by solving two linear equations.

Example. 4.1 The initial rate data at 30^0 C obtained for a reaction A + B → C + D is given the following table. Find a rate equation. Find the rate law for the following reaction at 300K.

Run Number	C_{A0} ,mol/L	C_{B0}, mol/L	$-r_{A0}$, mol/(L)(sec)
1	1.125	2.250	9.2
2	1.125	1.125	3.58
3	2.250	2.250	36.78

Solution: let the rate equation is $-r_A = k\ C_A^n\ C_B^m$

It is seen in Run 1 and 2, that C_{A0} is constant.

Therefore, $-r_{A01}/-r_{A02} = 9.2/3.58 = (1.125/1.125)^n(2.25/1.125)^m$

$2.008 = (1)^n(2)^m$ or, $2^1=2^m$ or, $m = 1$

Solution to Ex-1

- Similarly, from Run 1 and 3 C_{B0} is constant.

$$-r_{A03}/-r_{A01} = 36.78/9.2 = (1.125/2.25)^n(2.25/2.25)^m$$
$$3.997 = (2)^n(1)^m \text{ or}, 2^2 = 2^n \text{ or}, n = 2$$

So, the rate equation is $-r_A = k\, C_A^2\, C_B^1$

Substituting the data of Run1 in the rate equation it results,

$$9.2 = k(1.125)^2(2.25) \text{ or}, k = 0.306(mol/L)^{-2}s^{-1}$$

Therefore, the rate law is $-r_A = 0.306\, C_A^2 C_B mol L^{-1}s^{-1}$

The overall order of the reaction is 3 and the rate constant is $0.306(mol/L)^{-2}s^{-1}$.

[B] Numerical Method.

- The numerical differentiation method also may be used to find the derivative $\frac{dC_A}{dt}$.

- By tailor series expansion of a function $(x + h)$ about x is

- $(x_0 + h) = (x_0) + hf'(x_0) + \frac{h^2}{2}f''(\xi)$ where, $\xi \in (x_0, x_0 +$

Numerical Method

- the simple approximated first derivative at x_0 is obtained by from eq.(22) with replacing h by Δx and neglecting the truncation error term

$$f'(x_0) = \frac{(x_0 + \Delta x) - (x_0)}{\Delta x} \qquad (23)$$

- The eq.(4.23) is called forward differencing method. Similarly, in backward differencing method, the approximate equation will be

$$f'(x_0) = \frac{(x_0) - (x_0 - \Delta x)}{\Delta x} \qquad (24)$$

- The more accurate method is finding derivative based on two points $(x_0 - \Delta x)$ and $(x_0 + \Delta x)$ and the approximate formula is called centered difference method as

$$f'(x_0) = \frac{(x_0 + \Delta x) - (x_0 - \Delta x)}{2\Delta x} \qquad (25)$$

Numerical Method

However, a three point method may be used to evaluate the derivative at the end points, such at the initial time, t= 0 . The three point method for first derivative can be calculated by the equation.

$$y'(x) = \frac{-3 * y(x) + 4 * y(x + h) - y(x + 2h)}{2 * h}$$

(26)

At t=0, initial rate

$$-r_{A0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$$

(27)

Where, $\Delta t = t_2 - t_1 = t_1 - t_0$

Polynomial Adjusted Method

- A polynomial can be fitted with the batch reactor data of C_A versus t as
- $C_A = \alpha + \beta t + \gamma t^2 + \delta t^3 + \ldots\ldots + \mu t^N$ (28)
- Where the coefficients α, β, γ, δ,............μ are known.
- The rates at a different time may also be determined from the derivative at various times of the above polynomial
- By differentiating the equation $C_A = f(t)$ with respect to t we have
- $\frac{dC_A}{dt} = \beta + 2\gamma t + 3\delta t^2 + \cdots + \mu N t^{N-1}$ (29)
- Then the differentials at various t can be calculated by substituting different t-values.

Example 1 In hydrogen-Iodine gas-phase reaction, the variation of hydrogen concentration is recorded as a function time.

- $H_2 + I_2 \rightarrow 2HI \qquad C_A = [H_2]$
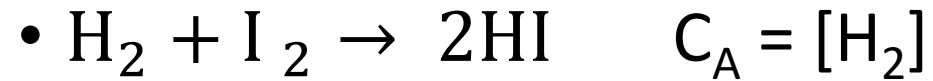
t, min	C_A, mol/L	t, min	C_A, mol/L
0	1.02	1.2	0.242
0.2	0.775	1.4	0.197
0.4	0.6	1.6	0.165
0.6	0.468	1.8	0.138
0.8	0.368	2.0	0.12
1	0.295		

- Calculate the initial reaction rate and rate at 0.6 min time.
- Find a rate equation by differential method of analysis.
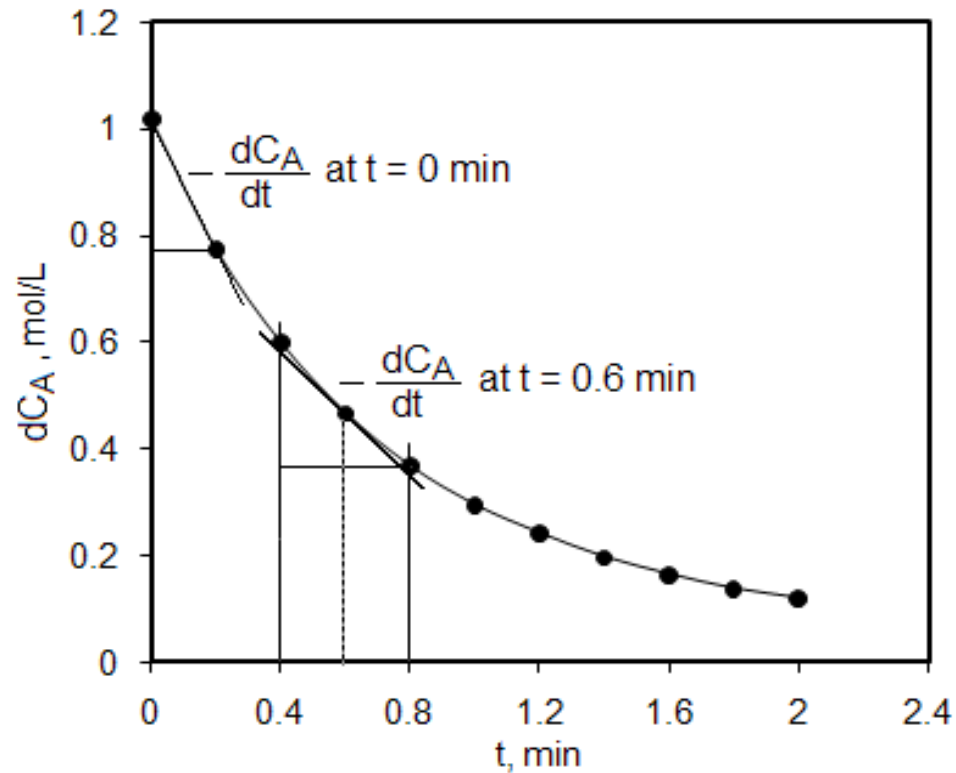
Concentration versus time plot

- Rate calculated by graphical method

- At t = 0 min, $\dfrac{-\Delta C_A}{\Delta t} = -(1.02 - 0.775)/0.2 = 1.225 \ \dfrac{mol}{min.L}$

- At t = 0.6 min, $\dfrac{-\Delta C_A}{\Delta t} = (0.368 - 0.6)/0.4 = 0.58 \ \dfrac{mol}{min.L}$

- Numerically,

- $At \ t = 0 \ min, -r_{A0} = \dfrac{-3C_{A0}+4C_{A1}-C_{A2}}{2\Delta t} = \dfrac{-3\times1.02+4\times0.775-0.6}{2\times0.2} =$ $-1.4 \ \dfrac{mol}{min.L}$

- By fitting the rate data in a polynomial using Matlab,

- $C_A = 0.0577 \ t^4 - 0.3672 \ t^3 - 0.9708 \ t^2 - 1.3840 \ t + 1.0189$

- $- dC_A/dt = 0.2309 \ t^3 - 1.1015 \ t^2 + 1.9415 \ t - 1.3840$

- Then the concentration and derivative at various time, t are calculated from the equation

t, min	C_A, mol/L	$-r_A$, mol/L.min
0.0000	1.0189	1.3840
0.2000	0.7781	1.0379
0.4000	0.5986	0.7689
0.6000	0.4661	0.5658
0.8000	0.3686	0.4175
1.0000	0.2962	0.3130
1.2000	0.2412	0.2413
1.4000	0.1982	0.1911
1.6000	0.1641	0.1515
1.8000	0.1377	0.1113

- $\ln(C_A)$ and $\ln(-r_A)$ are plotted in x and y co-ordinates respectively. Where the slope (p) and intercept $(\ln k)$ are found to be 1.2518 0.3547 respectively.

- $\mathrm{Order}, p \ = \ 1.2518, \ \ \mathrm{rate \ constant} \ = \ 1.4258 \ \mathrm{mol/min.\,L}$

- The initial rate at t= 0 is 1.3840 mol/L.min.

- The rate constant may also be calculated from the initial rate

- $\mathrm{k} = \dfrac{-r_A}{(C_{A0})^{1.252}} = \dfrac{1.3840}{(1.0189)^{1.252}} = 1.3519. \ \mathrm{mol/min.L}$
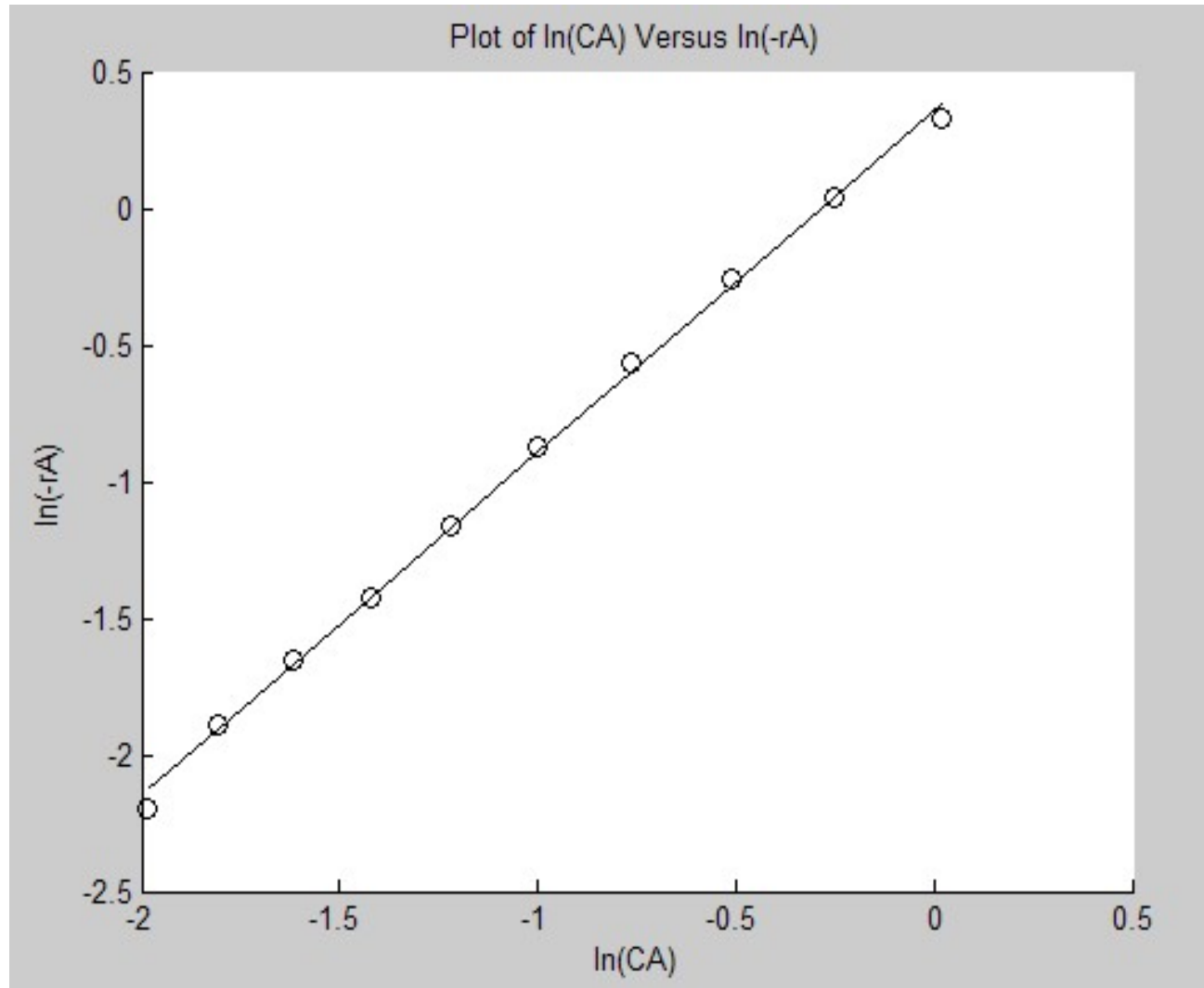
- The initial rate from the numerical method is 1.4 mol/min.L

Fig.7 ln(-r$_A$) versus ln(C$_A$) plot

Integral Method of Analysis

We may consider the empirical rate equation as

- $-r_A = kC_A^p \qquad where, p \neq 1$

- The rate equation is substituted in the batch reactor mole balance

- $-r_A = -\dfrac{1}{V}\dfrac{dN_A}{dt} = -\dfrac{dC_A}{dt} = kC_A^p$

- On integration of the above equation with the limits from $t = 0$, $C_A = C_{A0}$ to $t = t$, $C_A = C_A$ one may obtain

- $\displaystyle\int_{C_{A0}}^{C_A} \dfrac{dC_A}{kC_A^p} = \int_0^t dt$ $\qquad\qquad\qquad$ (30)

- $\dfrac{1}{C_A^{p-1}} - \dfrac{1}{C_{A0}^{n-1}} = (p-1)kt$ $\qquad\qquad\qquad$ (31)

- For a known value of p, and $p \neq 1$,

Integral Method of Analysis

- If we know the order p, the left-hand side function $(1/C_A^{p-1} - 1/C_{A0}^{p-1})$ is plotted against t for determining k from the slope.

- The integration method may be used for order of reaction, p= 0, 0.5, 1,2 3 so on

- In case of second-order reaction (p= 2) in eq.(31)

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \qquad (32)$$

- So, the $\frac{1}{C_A}$ versus t plot will be straight line. From the slope, the rate constant k can be calculated.

- For an example, a third-order reaction where p=3 , the integration results

$$\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 2kt \qquad (33)$$

Zero-order reaction

- The zero-order kinetics is written as

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = k \qquad\qquad (34)$$

- For constant volume process , $C_A = N_A/V$

- It may be written as $\quad -\frac{dC_A}{dt} = k$

- On integration from $\quad t = 0$, $C_A = C_{A0}$ to $t = t,\ C_A = C_A$, it results

- $C_A = C_{A0} - kt$, which is a straight line equation $y = mx + c'$ with slope, $m = -k$ and intercept, $c' = C_{A0}$.

- At a very large time as t $\rightarrow \infty$, C_A approaches to a negative value, which is never be possible as concentration cannot be negative.

- Hence, the equation is valid up to $t = C_{A0}/k$ at which $C_A = 0$.