CHAPTER 7 –
COLLECTION AND ANALYSIS OF RATE DATA

> **You can observe a lot just by watching.**
>
> *Yogi Berra, New York **Yankees***

Learning Outcomes

- After completing chapter 5, you will be able to
  - Determine the reaction order and specific reaction rate from experimental data obtained from either batch or flow reactors.
  - Describe how to use equal-area differentiation, polynomial fitting, numerical difference formulas and regression to analyze experimental data to determine the rate law.
  - Use regression software to evaluate the rate law parameters given experimental data.
  - Describe how the methods of half lives, and of initial rate, are used to analyze rate data.

Integral Method

Consider the following reaction that occurs in a constant volume Batch Reactor: (We will withdraw samples and record the concentration of A as a function of time.)

A → Products

Mole Balances: $$\frac{dN_A}{dt} = r_A V$$

Rate Laws: $$-r_A = kC_A^{\alpha}$$

Stoichiometry: $$V = V_0$$

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

Integral Method

Finally we should also use the formula to plot reaction rate data in terms of conversion vs. time for 0, 1st and 2nd order reactions.

Derivation equations used to plot 0th, 1st and 2nd order reactions.

These types of plots are usually used to determine the values k for runs at various temperatures and then used to determine the activation energy.

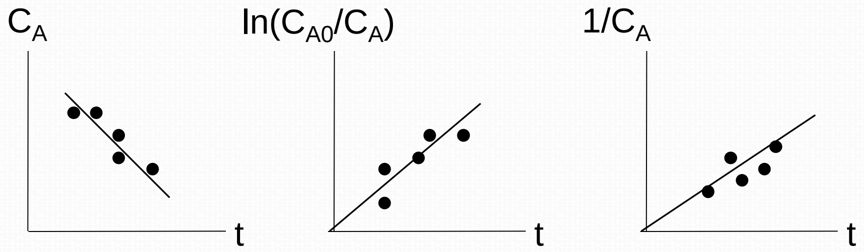
Zeroth order	**First Order**	**Second Order**
$\frac{dC_A}{dt} = r_A = -k$	$\frac{dC_A}{dt} = r_A = -kC_A$	$\frac{dC_A}{dt} = r_A = -kC_A^2$
$at \;\; t = 0, \;\; C_A = C_{A0}$	$at \;\; t = 0, \;\; C_A = C_{A0}$	$at \;\; t = 0, \;\; C_A = C_{A0}$
$\Rightarrow C_A = C_{A0} - kt$	$\Rightarrow \ln\left(\frac{C_{A0}}{C_A}\right) = kt$	$\Rightarrow \frac{1}{C_A} - \frac{1}{C_{A0}} = kt$

Integral Method

Guess and check for α = 0, 1, 2 and check against experimental plot.

$\alpha = 0$ $\quad$ $\alpha = 1$ $\quad$ $\alpha = 2$

$r_A = C_{A0} - kt$ $\quad$ $\ln\left(\frac{C_{A0}}{C_A}\right) = kt$ $\quad$ $\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$



Integral Method

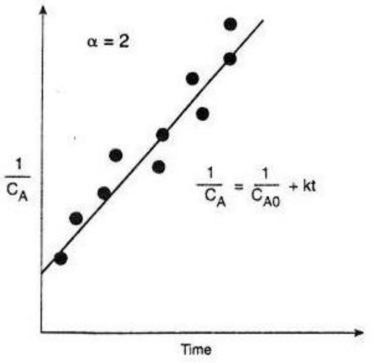


Figure 5-5 Second-order reaction.

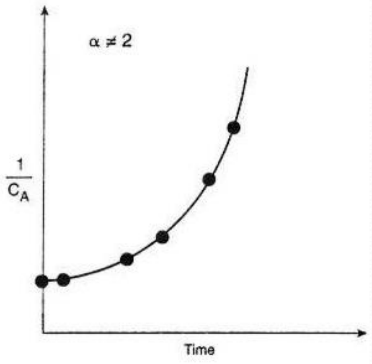


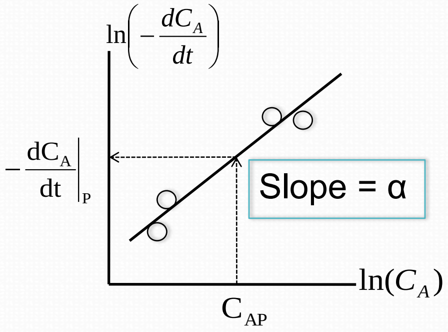
Figure 5-6 Plot of reciprocal concentration as a function of time.

Differential Method

Taking the natural log of $\left[-\frac{dC_A}{dt} = kC_A^{\alpha}\right]$

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

The reaction order can be found from a ln-ln plot of: $\left(-\frac{dC_A}{dt}\right)$ vs C_A



$$k = \frac{\left(-\frac{dC_A}{dt}\right)\Big|_p}{C_{Ap}^{\alpha}}$$

Differential Method

We are usually given concentration as a function of time from batch reactor experiments:

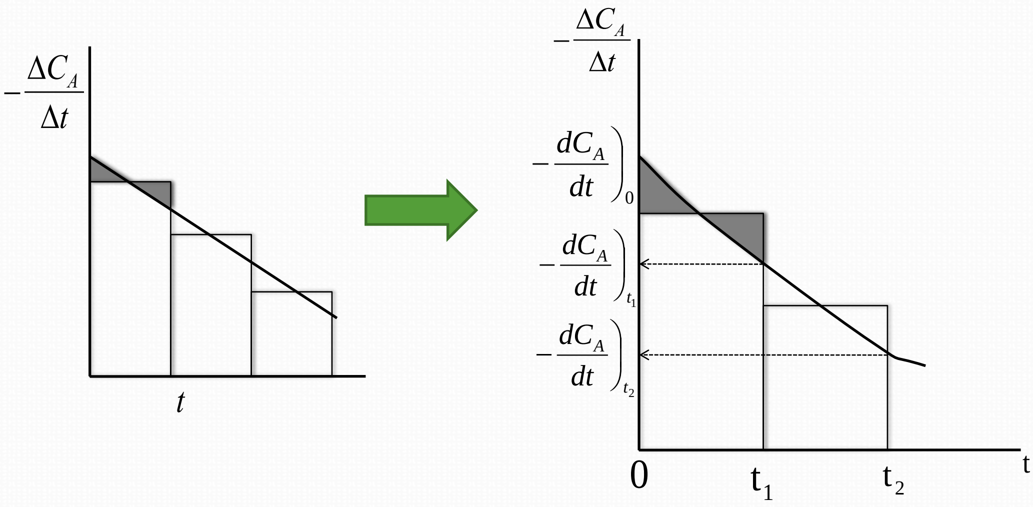
time (s)	0	t_1	t_2	t_3
Concentration (moles/dm^3)	C_{A0}	C_{A1}	C_{A2}	C_{A3}

Three ways to determine ($-dC_A/dt$) from concentration-time data:

1. Graphical differentiation
2. Numerical differentiation formulas
3. Differentiation of a polynomial fit to the data

Differential Method

1. Graphical Differentiation

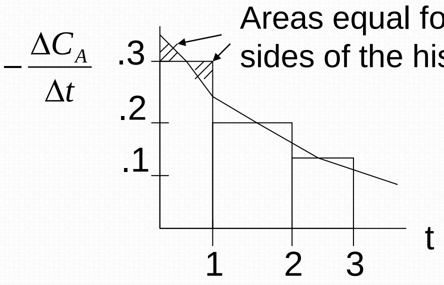


The method accentuates measurement error!

Example –

Finding the Rate Law

t(min)	0	1	2	3
C_A(mol/L)	1	0.7	0.5	0.35
$-\frac{\Delta C_A}{\Delta t}$	0.3	0.2	0.15	



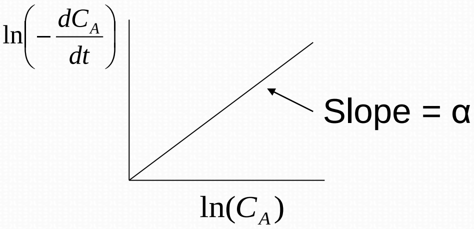
Areas equal for both sides of the histogram

Example –
Finding the Rate Law

Find f(t) of $-\frac{\Delta C_A}{\Delta t}$ using equal area differentiation

C_A	1	0.7	0.5	0.35
$-dC_A/dt$	0.35	0.25	0.175	0.12

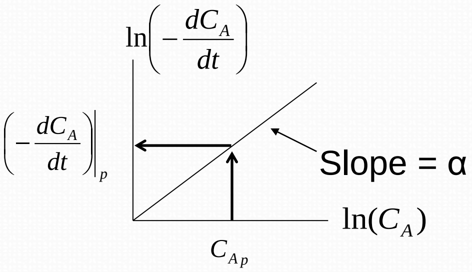
Plot ln($-dC_A/dt$) as a function of ln(C_A)



Example –
Finding the Rate Law

Choose a point, p, and find the concentration and derivative at that point to determine k.

$$k = \frac{\left.\left(-\frac{dC_A}{dt}\right)\right|_p}{C_{Ap}^{\alpha}}$$



Differential Method

2. Numerical differentiation formulas

Time (min)	t_0	t_1	t_2	t_3	t_4	t_5
Concentration (mol/dm^3)	C_{A0}	C_{A1}	C_{A2}	C_{A3}	C_{A4}	C_{A5}

The three-point differentiation formulas[1]

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

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

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

Differential Method

3. Differentiation of a Polynomial Fit

Time (min)	t_0	t_1	t_2	t_3	t_4	t_5
Concentration (mol/dm^3)	C_{A0}	C_{A1}	C_{A2}	C_{A3}	C_{A4}	C_{A5}

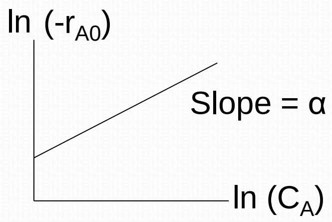
$$C_A = a_0 + a_1 t + a_2 t^2 + \cdots + a_n t^n$$

$$\frac{dC_A}{dt} = a_1 + 2a_2 t + 3a_3 t^2 + \cdots + n a_n t^{n-1}$$

Method of Initial Rates

- Used mainly for reversible reactions, why?
- A series of experiments is carried out at different initial concentrations, C_{A0}, and the initial rate of reactions, $-r_{A0}$, is determined for each run.

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



Method of Half-Lives

- The half-life of a reaction, $t_{1/2}$, is defined as the time it takes for the concentration of the reactant to fall to half of its initial value.
- By determining the half-life of a reaction as a function of the initial concentration, the reaction order and specific reaction rate can be determined.
- **If two reactants are involved in the chemical reaction, the experimenter will use the method of excess in conjunction with the method of half-lives to arrange the rate law in *the* form**

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

Method of Half-Lives

$$-r_A = kC_A^\alpha$$

- Mole balance on species A in a constant-volume batch reaction system combined with the rate law results in the following expression:

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

- **Only if $\alpha \neq 1$**, integrating with the initial condition $C_A = C_{A0}$ when *t* = 0, we find that

$$t = \frac{1}{k(1-\alpha)}\left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}}\right)$$

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

Method of Half-Lives

$$t = \frac{1}{k(1-\alpha)}\left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}}\right)$$

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

- Substituting with the half-life value, $C_A = ½\ C_{A0}$ when *t* = $t_{1/2}$, we get

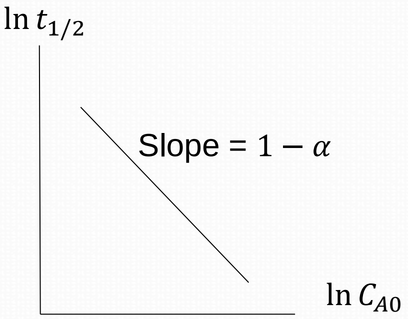
$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k(1-\alpha)}\left(\frac{1}{C_{A0}^{\alpha-1}}\right)$$

- And taking the natural log of both sides:

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

Method of Half-Lives

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



Method of Half-Lives

- **Only if $\alpha \neq 1$**

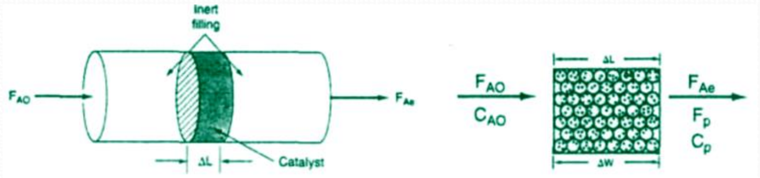
$$\ln t_{1/2} = \ln \frac{2^{\alpha-1}-1}{k(\alpha-1)} + (1-\alpha)\ln C_{A0}$$

- **What is the half-life of a first order reaction?**

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

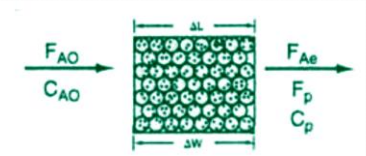
Differential Reactors

- A **differential reactor** is normally used to determine the rate of reaction as a function of either concentration or partial pressure.
- It consists of a tube containing a very small amount of catalyst usually arranged in the form of a thin wafer or disk.



Differential Reactors

$$A \rightarrow P$$



- **Mole Balance:**
  - The differential reactor is assumed to be ***gradientless**, so* the design equation will be similar to the CSTR design equation.

$$F_{A0} - F_{Ae} + r'_A . \Delta W = 0$$

$$-r'_A = \frac{F_{A0} - F_{Ae}}{\Delta W} = \frac{v_0 C_{A0} - v C_{Ae}}{\Delta W}$$

- **In terms of conversion:**

$$-r'_A = \frac{F_{A0} X}{\Delta W} = \frac{F_P}{\Delta W} = \frac{v_0 C_P}{\Delta W} \; (only\ for\ constant\ v)$$

Study Example 7-4