Chapter 5 Collection and Analysis of Rate Data

Focus on ways of obtaining and analyzing reaction rate data to obtain the rate law.

* batch reactor : homogeneous reactions
* differential reactor : solid-fluid reactions

Six methods of analyzing the data :

- differential method
- integral method
- method of half-lives
- method of initial rates
- linear regression
- nonlinear regression

} least-squares analysis

5.1 Batch Reactor Data

$$\text{Conc. vs. time} \xrightarrow[\text{or least squares}]{\text{differential} \atop \text{integral}} \text{reaction order, specific rxn rate}$$

5.1.1 Differential Method of Rate Analysis

* rxn rate is a function of the conc. of <u>one reactant</u>

$$A \longrightarrow \text{products}$$

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

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heterogeneous reactions, we need to have an understanding of the reaction and possible mechanisms in order to postulate the rate law in Step 6B. After studying Chapter 10 on heterogeneous reactions, one will be able to postulate different rate laws and then use Polymath nonlinear regression to choose the "best" rate law and reaction rate parameters.

The procedure we should use to delineate the rate law and rate law parameters is given in Table 5-1.

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TABLE 5-1. STEPS IN ANALYZING RATE DATA

1. **Postulate a rate law.**
   A. Power law models for homogeneous reactions

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

   B. Langmuir-Hinshelwood models for heterogeneous reactions

$$-r_A' = \frac{kP_A}{1+K_AP_A}, \quad -r_A' = \frac{kP_AP_B}{(1+K_AP_A+P_B)^2}$$

2. **Select reactor type and corresponding mole balance.**
   A. If batch reactor (Section 5.2), use mole balance on Reactant A

$$-r_A = -\frac{dC_A}{dt} \qquad \text{(TE5-1.1)}$$

   B. If differential PBR (Section 5.5), use mole balance on Product P (A → P)

$$-r_A' = \frac{F_P}{\Delta W} = C_P v_0/\Delta W \qquad \text{(TE5-1.2)}$$

3. **Process your data in terms of measured variable** (e.g., N_A, C_A, or P_A). If necessary, rewrite your mole balance in terms of the measured variable (e.g., P_A).
4. **Look for simplifications.** For example, if one of the reactants is in excess, assume its concentration is constant. If the gas phase mole fraction of reactant A is small, set $\varepsilon \approx 0$.
5. **For a batch reactor, calculate $-r_A$ as a function of concentration C_A to determine reaction order.**
   A. Differential analysis
   Combine the mole balance (TE5-1.1) and power law model (TE5-1.3).

$$-r_A = kC_A^{\alpha} \qquad \text{(TE5-1.3)}$$

$$-\frac{dC_A}{dt} = kC_A^{\alpha} \qquad \text{(TE5-1.4)}$$

and then take the natural log.

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(-r_A) = \ln k + \alpha \ln C_A \qquad \text{(TE5-1.5)}$$

(1) Find $-\frac{dC_A}{dt}$ from C_A versus t data by

(a) Graphical method
(b) Finite differential method
(c) Polynominal

(2) Plot $\ln\left(-\frac{dC_A}{dt}\right)$ versus $\ln C_A$ and find reaction order α, which is the slope of the line fit to the data.

(3) Find k.

B. Integral method

For $-r_A = kC_A^{\alpha}$, the combined mole balance and rate law is

$$-\frac{dC_A}{dt} = kC_A^{\alpha} \qquad \text{(TE5-1.4)}$$

(1) Guess α and integrate Equation (TE5-1.4). Rearrange your equation to obtain the appropriate function of C_A, which when plotted as a function of time should be linear. If it is linear, then the guessed value of α is correct and the slope is the specific reaction rate, k. If it is not linear, guess again for α. If you guess $\alpha = 0$, 1, and 2 and none of theses orders fit the data, proceed to nonlinear reression.

(2) Nonlinear regression (Polymath)

Integrate Equation (TE5-1.4) to obtain

$$t = \frac{1}{k}\left[\frac{C_{A0}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)}\right] \text{ for } \alpha \neq 1 \qquad \text{(TE5-1.6)}$$

Use Polymath regression to find α and k. A Polymath tutorial on regression with screen shots is shown in the Chapter 5 *Summary Notes* on the CD-ROM and web.

6. For differential PBR calculate $-r'_A$ as a function of C_A or P_A

A. Calculate $-r'_A = \frac{v_0 C_P}{\Delta W}$ as a function of reactant concentration, C_A.

B. Choose model (see Chapter 10), e.g.,

$$-r'_A = \frac{kP_A}{1 + K_A P_A}$$

C. Use nonlinear regression to find the best model and model parameters. See example on the CD-ROM *Summary Notes* using data from heterogeneous catalysis, Chapter 10.

7. **Analyze your rate law model for "goodness of fit."** Calculate a correlation coefficient.

然而, for

$$A + B \longrightarrow \text{products}$$

method of excess should be used.

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

$\boxed{\text{a large excess of B}}$ $= k' C_A^{\alpha}$ 其中 $k' = k_A C_B^{\beta} \approx k_A C_{B0}^{\beta}$

or

$\boxed{\text{a large excess of A}}$ $= k'' C_B^{\beta}$ 其中 $k'' = k_A C_A^{\alpha} \approx k_A C_{A0}^{\alpha}$

Once α and β are determined,

$$k_A = \frac{-r_A}{C_A^{\alpha} C_B^{\beta}} \quad \left[\left(\frac{dm^3}{mol}\right)^{\alpha+\beta-1} \cdot s^{-1} \right]$$

at specified conc. of C_A and C_B

* in a constant-volume batch reactor

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

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

Plot $\ln\left(-\frac{dC_A}{dt}\right)$ vs. $\ln C_A$ $\Longrightarrow$ α, k_A

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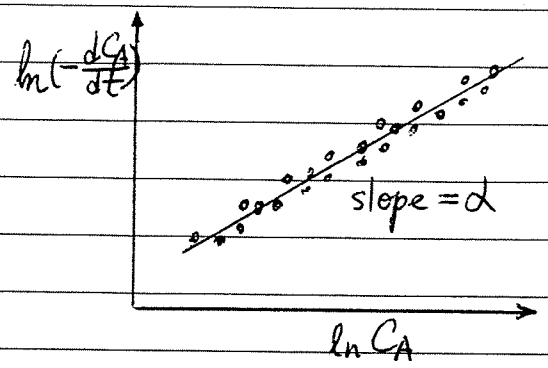

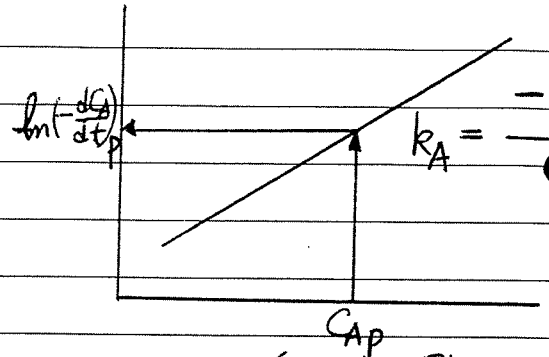

$$k_A = \frac{-\left.\frac{dC_A}{dt}\right|_p}{(C_{Ap})^\alpha}$$

線上任意一點

* 在 differential method 中，獲得 $\underbrace{\text{正確的} -dC_A/dt}_{\text{from } C_A \text{ vs. } t}$ 很重要

方法：

a. Graphical Method

see Appendix A.2

b. Numerical Method: for $\Delta t = t_1 - t_0 = t_2 - t_1 = \cdots\cdots$

ex.

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

the three-point differentiation formulas

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

interior pt. $\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t}\left[C_{A(i+1)} - C_{A(i-1)}\right]$ e.g. $\left(\frac{dC_A}{dt}\right)_{t_3} = \frac{1}{2\Delta t}\left[C_{A4} - C_{A2}\right]$

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

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c. Polynomial Fit

$$C_A \text{ vs. time} \xrightarrow{PC} C_A = \underbrace{a_0 + a_1 t + a_2 t^2 + \cdots + a_n t^n}_{\text{order 的選定很重要}}$$

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

5.2.1D Finding the Rate Law Parameters

Now, using either the graphical method, differentiation formulas, or the polynomial derivative, the following table can be set up:

Time	t_0	t_1	t_2	t_3
Concentration	C_{A0}	C_{A1}	C_{A2}	C_{A3}
Derivative	$\left(-\frac{dC_A}{dt}\right)_0$	$\left(-\frac{dC_A}{dt}\right)_1$	$\left(-\frac{dC_A}{dt}\right)_2$	$\left(-\frac{dC_A}{dt}\right)_3$

The reaction order can now be found from a plot of $\ln(-dC_A/dt)$ as a function of $\ln C_A$, as shown in Figure 5-1(a), since

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k_A + \alpha \ln C_A \tag{5-7}$$

Before solving an example problem review the steps to determine the reaction rate law from a set of data points (Table 5-1).

Example 5–1 Determining the Rate Law

The reaction of triphenyl methyl chloride (trityl) (A) and methanol (B)

$$(C_6H_5)_3CCl + CH_3OH \rightarrow (C_6H_5)_3C\overset{\overset{\displaystyle O}{\|}}{C}H_3 + HCl$$

$$A \quad + \quad B \quad \rightarrow \quad C \quad + D$$

was carried out in a solution of benzene and pyridine at 25°C. Pyridine reacts with HCl that then precipitates as pyridine hydrochloride thereby making the reaction irreversible.

The concentration-time data in Table E5-1.1 was obtained in a batch reactor

TABLE E5-1.1. RAW DATA

Time (min)	0	50	100	150	200	250	300
Concentration of A (mol/dm^3) × 10^3	50	38	30.6	25.6	22.2	19.5	17.4

(At $t = 0$, $C_A = 0.05\ M$)

The initial concentration of methanol was 0.5 mol/dm^3.

Part (1) Determine the reaction order with respect to triphenyl methyl chloride.

Part (2) In a separate set of experiments, the reaction order wrt methanol was found to be first order. Determine the specific reaction rate constant.

Solution

Part (1) Find reaction order wrt trityl.

Step 1 Postulate a rate law.

$$-r_A = kC_A^\alpha C_B^\beta \tag{E5-1.1}$$

Step 2 Process your data in terms of the measured variable, which in this case is C_A.

Step 3 Look for simplifications. Because the concentration of methanol is 10 times the initial concentration of triphenyl methyl chloride, its concentration is essentially constant

$$C_B = C_{B0} \tag{E5-1.2}$$

Substituting for C_B in Equation (E5-1.1)

$$-r_A = \underbrace{kC_{B0}^\beta}_{k'} C_A^\alpha$$

$$-r_A = k' C_A^\alpha \tag{E5-1.3}$$

Step 4 Apply the CRE algorithm

Mole Balance

$$\frac{dN_A}{dt} = r_A V \tag{E5-1.4}$$

Rate Law

$$-r_A = k' C_A^\alpha \tag{E5-1.3}$$

Stoichiometry: Liquid

$$V = V_0 \tag{E5-1.4}$$

$$C_A = \frac{N_A}{V_0}$$

Combine: Mole balance, rate law, and stoichiometry

$$-\frac{dC_A}{dt} = k' C_A^{\alpha} \tag{E5-1.5}$$

Taking the natural log of both sides of Equation (E5-1.5)

$$\ln\left[-\frac{dC_A}{dt}\right] = \ln k' + \alpha \ln C_A \tag{E5-1.6}$$

The slope of a plot of $\ln\left[-\frac{dC_A}{dt}\right]$ versus $\ln C_A$ will yield the reaction order α with respect to triphenyl methyl chloride (A).

Step 5 Find $\left[-\frac{dC_A}{dt}\right]$ as a function of C_A from concentration-time data.

We will find $\left(-\frac{dC_A}{dt}\right)$ by each of the three methods just discussed, the graphical, finite difference, and polynomial methods.

Step 5A.1a ***Graphical Method.*** We now construct Table E5-1.2.

TABLE E5–1.2 PROCESSED DATA

t (min)	$C_A \times 10^3$ (mol/dm^3)	$-\frac{\Delta C_A}{\Delta t} \times 10^4$ (mol/dm^3 · min)	$-\frac{dC_A}{dt} \times 10^4$ (mol/dm^3 · min)
0	50		3.0
		2.40[a]	
50	38		1.86
		1.48	
100	30.6		1.2
		1.00	
150	25.6		0.8
		0.68	
200	22.2		0.5
		0.54	
250	19.5		0.47
		0.42	
300	17.4		

[a]

$$-\frac{\Delta C_A}{\Delta t} = -\frac{C_{A2} - C_{A1}}{t_2 - t_1} = -\left(\frac{38-50}{50-0}\right) \times 10^{-3} = 0.24 \times 10^{-3} = 2.4 \times 10^{-4} (\text{mol/dm}^3 \cdot \text{min})$$

The derivative $-dC_A/dt$ is determined by calculating and plotting $(-\Delta C_A/\Delta t)$ as a function of time, t, and then using the equal-area differentiation technique (Appendix A.2) to determine $(-dC_A/dt)$ as a function of C_A. First, we calculate the ratio $(-\Delta C_A/\Delta t)$ from the first two columns of Table E5-1.2; the result is written in the third column. Next we use Table E5-1.2 to plot the third column as a function of the

first column in Figure E5-1.1 [i.e., $(-\Delta C_A/\Delta t)$ versus t]. Using equal-area differentiation, the value of $(-dC_A/dt)$ is read off the figure (represented by the arrows); then it is used to complete the fourth column of Table E5-1.2.

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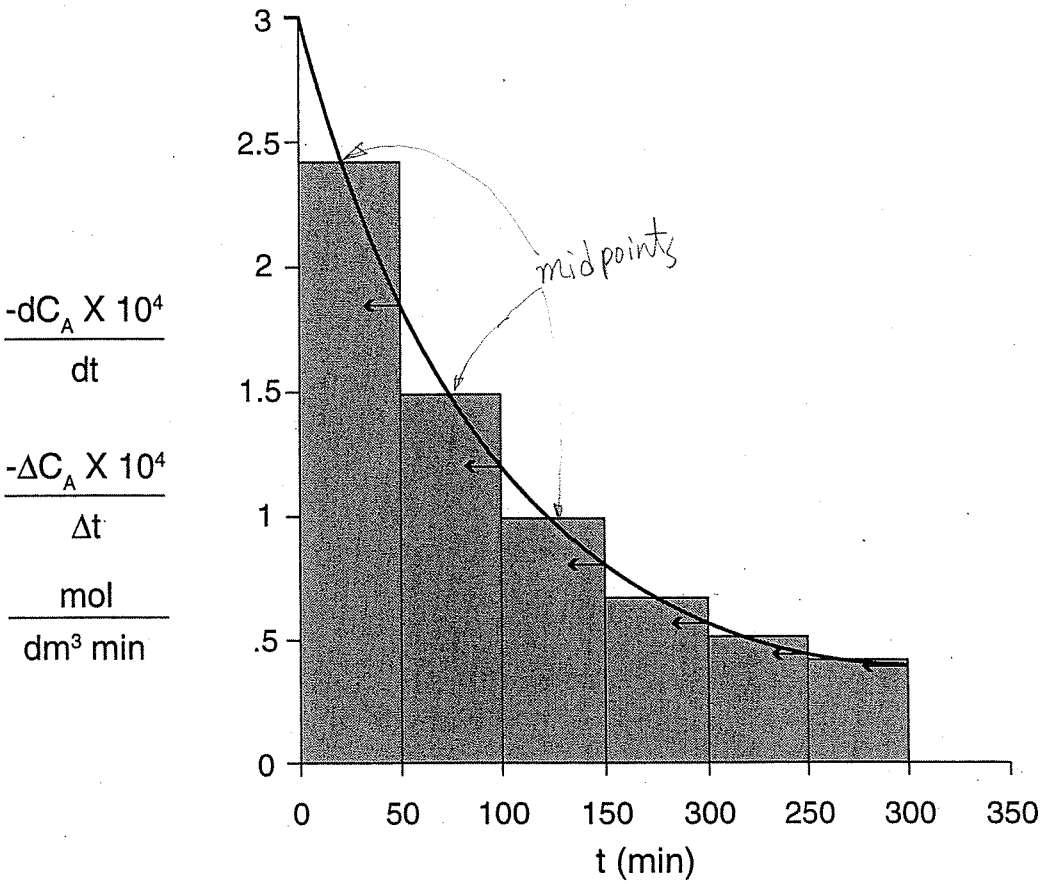


Figure E5-1.1 Graphical differentiation.

Step 5A.1b Finite Difference Method. We now calculate (dC_A/dt) using the finite difference formulas [i.e., Equations (5-8) through (5-10)].

$$t=0 \quad \left(\frac{dC_A}{dt}\right)_{t=0} = \frac{-3C_{A0}+4C_{A1}-C_{A2}}{2\Delta t}$$

$$= \frac{[-3(50)+4(38)-30.6]\times 10^{-3}}{100}$$

$$= -2.86\times 10^{-4}\ \text{mol/dm}^3\cdot\text{min}$$

$$-\frac{dC_A}{dt}\times 10^4 = 2.86\ \text{mol/dm}^3\cdot\text{min}$$

$$t=50 \quad \left(\frac{dC_A}{dt}\right)_1 = \frac{C_{A2}-C_{A0}}{2\Delta t} = \frac{(30.6-50)\times 10^{-3}}{100}$$

$$= -1.94\times 10^{-4}\ \text{mol/dm}^3\cdot\text{min}$$

$$t = 100 \quad \left(\frac{dC_A}{dt}\right)_2 = \frac{C_{A3} - C_{A1}}{2\Delta t} = \frac{(25.6 - 38) \times 10^{-3}}{100}$$
$$= -1.24 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 150 \quad \left(\frac{dC_A}{dt}\right)_3 = \frac{C_{A4} - C_{A2}}{2\Delta t} = \frac{(22.2 - 30.6) \times 10^{-3}}{100}$$
$$= -0.84 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 200 \quad \left(\frac{dC_A}{dt}\right)_4 = \frac{C_{A5} - C_{A3}}{2\Delta t} = \frac{(19.5 - 25.6) \times 10^{-3}}{100}$$
$$= -0.61 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 250 \quad \left(\frac{dC_A}{dt}\right)_5 = \frac{C_{A6} - C_{A4}}{2\Delta t} = \frac{(17.4 - 22.2) \times 10^{-3}}{100}$$
$$= -0.48 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

$$t = 300 \quad \left(\frac{dC_A}{dt}\right)_6 = \frac{C_{A4} - 4C_{A5} + 3C_{A6}}{2\Delta t} = \frac{[22.2 - 4(19.5) + 3(17.4)] \times 10^{-3}}{100}$$
$$= -0.36 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}$$

Summary Notes

Polymath turorial or fitting data can be found on the ummary Notes on the CD.

Step 5A.1c Polynomial Method. Another method to determine (dC_A/dt) is to fit the concentration of A to a polynomial in time and then to differentiate the resulting polynomial.

We will use the Polymath software package to express concentration as a function of time. Here we first choose the polynomial degree (in this case, fourth degree) and then type in the values of C_A at various times t to obtain

$$C_A = 0.04999 - 2.978 \times 10^{-4}t + 1.343 \times 10^{-6}t^2 - 3.485 \times 10^{-9}t^3 + 3.697 \times 10^{-12}t^4 \quad \text{(E5-1.7)}$$

C_A is in (mol/dm^3) and t is in minutes. A plot of C_A versus t and the corresponding fourth-degree polynomial fit are shown in Figure E5-1.2.

TABLE E5–1.3 POLYMATH OUTPUT

Linear Regression Report

Model: CA = a0 + a1*t + a2*t^2 + a3*t^3 + a4*t^4

Variable	Value	95% confidence
a0	0.0499903	3.1E-04
a1	-2.978E-04	1.762E-05
a2	1.343E-06	2.72E-07
a3	-3.485E-09	1.418E-09
a4	3.697E-12	2.347E-12

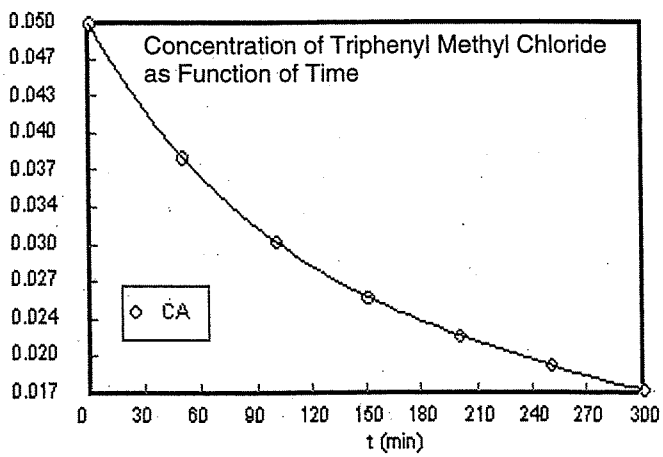


Figure E5-1.2 Polynomial fit.

Differentiating Equation (E5-1.7) yields

$$\frac{dC_A}{dt} \times 10^3 = -0.2987 + 0.002687t - 1.045 \times 10^{-5}t^2 + 1.479 \times 10^{-8}t^3 \qquad \text{(E5-1.8)}$$

Note: You can also obtain Equation (E5-1.9) directly from Polymath.

To find the derivative at various times, we substitute the appropriate time into Equation (E5-1.8) to arrive at the fourth column in Table E5-1.4 and multiply by (–1). We can see that there is quite a close agreement between the graphical technique, finite difference, and the polynomial methods.

TABLE E5-1.4. SUMMARY OF PROCESSED DATA

	Graphical	*Finite Difference*	*Polynominal*	
	$-\frac{dC_A}{dt} \times 10{,}000$	$-\frac{dC_A}{dt} \times 10{,}000$	$-\frac{dC_A}{dt} \times 10{,}000$	$C_A \times 1{,}000$
t (min)	(mol/dm³ · min)	(mol/dm³ · min)	(mol/dm³ · min)	(mol/dm³)
0	3.0	2.86	2.98	50
50	1.86	1.94	1.88	38
100	1.20	1.24	1.19	30.6
150	0.80	0.84	0.80	25.6
200	0.68	0.61	0.60	22.2
250	0.54	0.48	0.48	19.5
300	0.42	0.36	0.33	17.4

We will now plot columns 2, 3, and 4 $\left(-\frac{dC_A}{dt} \times 10{,}000\right)$ as a function of column 5 ($C_A \times 1{,}000$) on log-log paper as shown in Figure E5-1.3. We could also substitute the parameter values in Table E5-1.4 into Excel to find α and k'. Note that most of the points for all methods fall virtually on top of one another.

From Figure E5-1.3, we found the slope to be 2.05 so that the reaction is said to be second order wrt triphenyl methyl chloride. To evaluate k′, we can evaluate the derivative at $C_{Ap} = 20 \times 10^{-3}$ mol/dm³, which is

$$\left(-\frac{dC_A}{dt}\right)_p = 0.5 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \qquad \text{(E5-1.9)}$$

then

$$k' = \frac{\left(-\frac{dC_A}{dt}\right)_p}{C_{Ap}^2} \qquad \text{(E5-1.10)}$$

$$= \frac{0.5 \times 10^{-4} \text{mol/dm}^3 \cdot \text{min}}{(20 \times 10^{-3} \text{mol/dm}^3)^2} = 0.125 \text{ dm}^3 / \text{mol} \cdot \text{min}$$

As will be shown in Section 5-1.3, we could also use nonlinear regression on Equation (E5-1.7) to find k':

$$k' = 0.122 \text{ dm}^3/\text{mol} \cdot \text{min} \qquad \text{(E5-1.11)}$$

P. 5-12

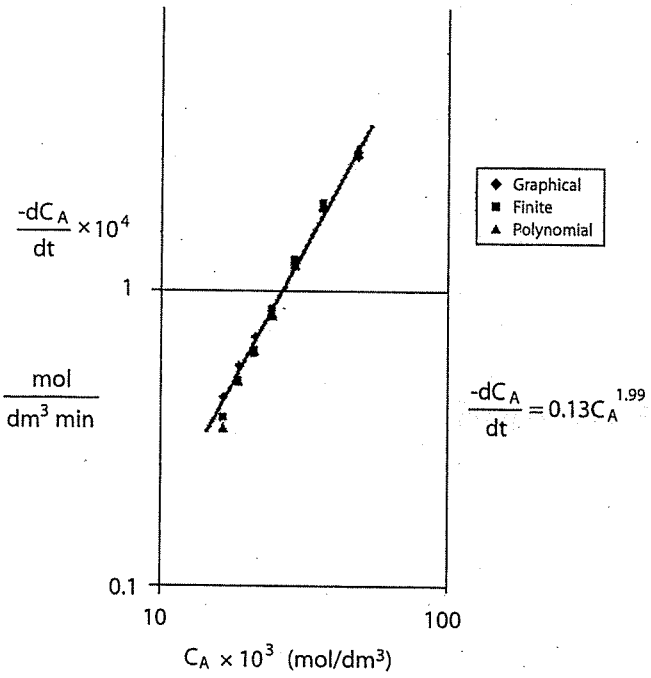


Figure E5-1.3 Excel plot to determine α and k.

The Excel graph shown in Figure E5-1.3 gives $\alpha = 1.99$ and $k' = 0.13$ dm³/mol · min. We could set $\alpha = 2$ and regress again to find $k' = 0.122$ dm³/mol · min.

ODE Regression. There are techniques and software becoming available whereby an ODE solver can be combined with a regression program to solve differential equations, such as

$$-\frac{dC_A}{dt} = k_A' C_A^{\alpha} \qquad \text{(E5-1.5)}$$

to find k_A and α from concentration–time data.

Part (2) The reaction was said to be first order wrt methanol, β = 1,

$$k' = C_{B0}^{\beta} k = C_{B0} k \qquad \text{(E5-1.12)}$$

Assuming C_{B0} is constant at 0.5 mol/dm³ and solving for k yields

$$k = \frac{k'}{C_{B0}} = \frac{0.122 \dfrac{dm^3}{mol \cdot min}}{0.5 \dfrac{mol}{dm^3}}$$

$$k = 0.244\ (dm^3/mol)^2 / min$$

The rate law is

$$\boxed{-r_A = [0.244(dm^3/mol)^2/min] C_A^2 C_B} \qquad \text{(E5-1.13)}$$

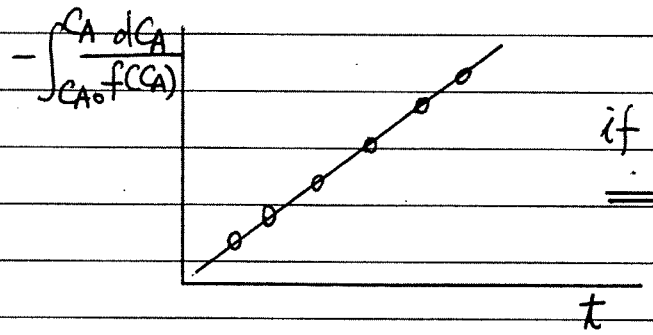
5.1.2 Integral Method

a rxn $A \longrightarrow$ products

in a constant-volume batch reactor

$$-\frac{dC_A}{dt} = -r_A = k \cdot \underbrace{f(C_A)}_{\text{guess the rxn order}}$$

$$\Rightarrow -\int_{C_{A0}}^{C_A} \frac{dC_A}{f(C_A)} = k \cdot t$$



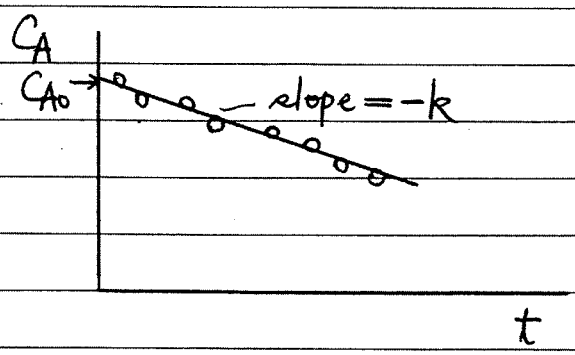
if the plot shows a linear relationship
$\Longrightarrow$ the rxn order is correct

若不是 linear plot, 須再試其他 order.

<u>Zero-order rxn</u>

$$-\frac{dC_A}{dt} = -r_A = k$$ rxn rate 與 conc. 無關

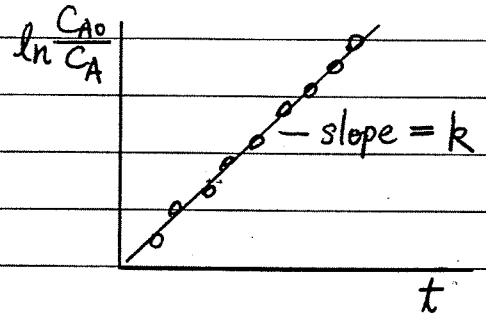
$$\Longrightarrow C_{A0} - C_A = kt \quad \text{or} \quad C_A = C_{A0} - kt$$



first-order rxn

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

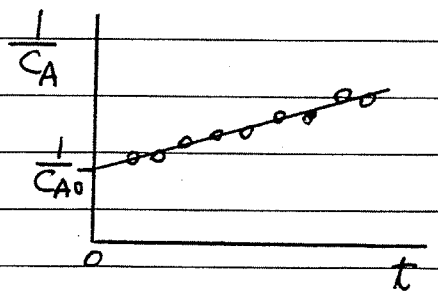
$$\Longrightarrow \quad \ln\frac{C_{A0}}{C_A} = kt$$



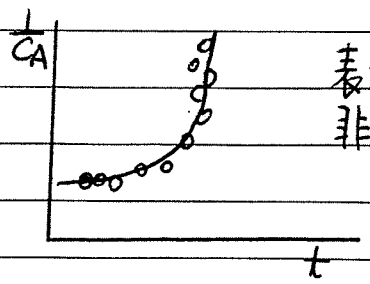
second-order rxn

$$-\frac{dC_A}{dt} = kC_A^2$$

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



若 plot 為



表示此 rxn
非 2nd-order

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out **not to be linear**, such as shown in Figure 5-6, we would say that the proposed reaction order did not fit the data. In the case of Figure 5-6, we would conclude the reaction is not second order. P.5-15

The idea is to range the data so that a linear relationship is obtained.

It is important to restate that, given a reaction rate law, you should be able to choose quickly the appropriate function of concentration or conversion that yields a straight line when plotted against time or space time.

Example 5–2 Integral Method of CRE Data Analysis

Use the integral method to confirm that the reaction is second order wrt triphenyl methyl chloride as described in Example 5-1 and to calculate the specific reaction rate k'

$$\text{Trityl (A)} + \text{Methanol (B)} \rightarrow \text{Products}$$

Solution

Substituting for $\alpha = 2$ in Equation (E5-1.5)

$$-\frac{dC_A}{dt} = k' C_A^{\alpha} \tag{E5-1.5}$$

we obtain

$$-\frac{dC_A}{dt} = k' C_A^2 \tag{E5-2.1}$$

Integrating with $C_A = C_{A0}$ at $t = 0$

$$t = \frac{1}{k'}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] \tag{E5-2.2}$$

Rearranging

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k't \tag{E5-2.3}$$

We see if the reaction is indeed second order then a plot of $(1/C_A)$ versus t should be linear. The data in Table E5-1.1 in Example 5-1 will be used to construct Table E5-2.1.

TABLE E5-2.1. PROCESSED DATA

t (min)	0	50	100	150	200	250	300
C_A (mol/dm^3)	0.05	0.038	0.0306	0.0256	0.0222	0.0195	0.0174
$1/C_A$ (dm^3/mol)	20	26.3	32.7	39.1	45	51.3	57.5

In a graphical solution, the data in Table E5-2.1 can be used to construct a plot of $1/C_A$ as a function of t, which will yield the specific reaction rate k'. This plot is shown in Figure E5-2.1. Again, one could use Excel or Polymath to find k' from the data in Table E5-2.1. The slope of the line is the specific reaction rate k'

P.5-16

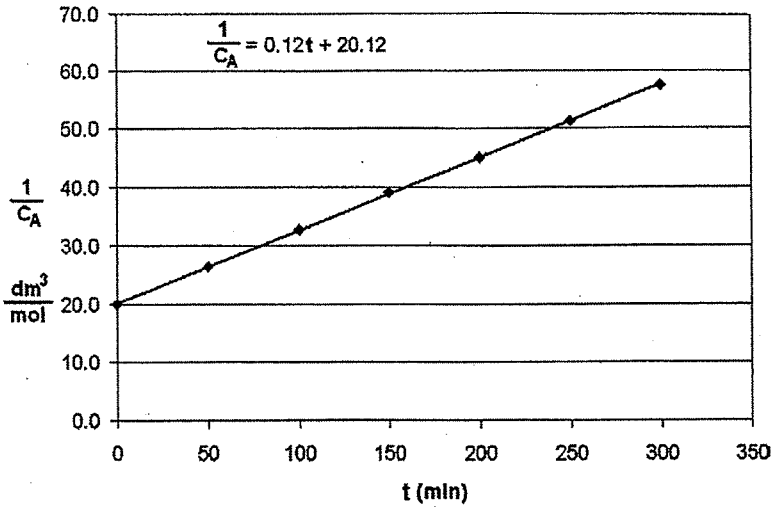


Figure E5-2.1 Plot of the reciprocal of C_A versus t for a second-order reaction.

We see from the Excel analysis and plot that the slope of the line is 0.12 dm³/mol · min.

$$k' = 0.12\ \frac{\text{dm}^3}{\text{mol}\cdot\text{min}}$$

Calculating k,

$$k = \frac{k'}{C_{B0}} = \frac{0.12}{0.5}\frac{\text{dm}^3/\text{mol/min}}{\text{mol/dm}^3} = 0.24\left(\frac{\text{dm}^3}{\text{mol}}\right)^2/\text{min}$$

The rate law is

$$-r_A = \left[0.24\left(\frac{\text{dm}^3}{\text{mol}}\right)^2/\text{min}\right]C_A^2 C_B$$

We note the integral method tends to smooth the data.

Polymath

An alternate computer solution would be to regress $\frac{1}{C_A}$ versus t with a software package such as Polymath.

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k't \qquad \text{(E5-2.4)}$$

Let CA inverse = $\frac{1}{C_A}$, $a_0 = \frac{1}{C_{A0}}$, and $a_1 = k'$ and then enter the data in Table E5-2.1.

Linear Regression Report

Model: CAinverse = a0 + a1*t

Variable	Value	95% confidence
a0	20.117525	0.225264
a1	0.124794	0.0012495

From the Polymath output, we obtain k' = 0.125 dm³/mol · min, which yields k = 0.25 dm³/mol · min. We shall discuss regression in Example 5-3.

Non-linear Regression 迴歸分析

P.5-17

We now integrate Equation (5-6) to give

Const-V BR

$$\frac{dC_A}{dt} = -kC_A^{\alpha} \quad (5\text{-}6) \qquad C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt$$

Rearranging to obtain the concentration as a function of time, we obtain

$$C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/(1-\alpha)} \tag{5-18}$$

Now we could use Polymath or MATLAB to find the values of α and k that would minimize the sum of squares of the differences between the measured and calculated concentrations. That is, for N data points,

$$s^2 = \sum_{i=1}^{N} (\underset{\text{measured}}{C_{Ami}} - \underset{\text{calculated}}{C_{Aci}})^2 = \sum_{i=1}^{N} \left[C_{Ami} - [C_{A0}^{1-\alpha} - (1-\alpha)kt_i]^{1/(1-\alpha)} \right]^2 \tag{5-19}$$

we want the values of α and k that will make s^2 a minimum.

If Polymath is used, one should use the absolute value for the term in brackets in Equation (5-19), that is,

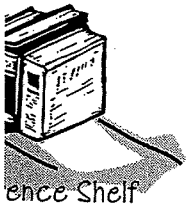
$$s^2 = \sum_{i=1}^{n} \left[C_{Ami} - \{(\text{abs}[C_{A0}^{1-\alpha} - (1-\alpha)kt_i]\}^{1/(1-\alpha)} \right]^2 \tag{5-20}$$

Another way to solve for the parameter values is to use time rather than concentrations:

$$\boxed{t_c = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k(1-\alpha)}} \tag{5-21}$$

That is, we find the values of k and α that minimize

$$s^2 = \sum_{i=1}^{N} (t_{mi} - t_{ci})^2 = \sum_{i=1}^{N} \left[t_{mi} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2 \tag{5-22}$$



Finally, a discussion of *weighted least squares* as applied to a first-order reaction is provided in the *Professional Reference Shelf R5.2* on the CD-ROM.

Example 5–3 Use of Regression to Find the Rate Law Parameters

We shall use the reaction and data in Example 5-1 to illustrate how to use regression to find α and k'.

$$(C_6H_5)_3CCl + CH_3OH \rightarrow (C_6H_5)_3COCH_3 + HCl$$

$$A \quad + \quad B \quad \rightarrow \quad C \quad + \quad D$$

The Polymath regression program is included on the CD-ROM. Recalling Equation (E5-1.5)

P.5-18

$$-\frac{dC_A}{dt} = k'C_A^{\alpha} \tag{E5-1.5}$$

and integrating with the initial condition when $t = 0$ and $C_A = C_{A0}$ for $\alpha \neq 1.0$

$$\boxed{t = \frac{1}{k'}\frac{C_{A0}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)}} \tag{E5-3.1}$$

Substituting for the initial concentration $C_{A0} = 0.05$ mol/dm^3

$$t = \frac{1}{k'}\frac{(0.05)^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \tag{E5-3.2}$$

Let's do a few calculations by hand to illustrate regression. We will first assume a value of α and k and then calculate t for the concentrations of A given in Table E5-1.1. We will then calculate the sum of the squares of the difference between the measured times t_m and the calculated times (i.e., s^2). For N measurements,

$$s^2 = \sum_{i=1}^{N}(t_{mi} - t_{ci})^2 = \sum_{i=1}^{N}\left(t_{mi} - \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k'(1-\alpha)}\right)^2$$

Our first guess is going to be $\alpha = 3$ and $k' = 5$, with $C_{A0} = 0.05$. Equation (E5-3.2) becomes

$$t_c = \frac{1}{2k'}\left[\frac{1}{C_A^2} - \frac{1}{C_{A0}^2}\right] = \frac{1}{10}\left[\frac{1}{C_A^2} - 400\right] \tag{E5-3.3}$$

We now make the calculations for each measurement of concentration and fill in columns 3 and 4 of Table E5-3.1. For example, when $C_A = 0.038$ mol/dm^3 then

$$t_{c1} = \frac{1}{10}\left[\frac{1}{(0.038)^2} - 400\right] = 29.2 \text{ min}$$

which is shown in Table E5-3.1 on line 2 for guess 1. We next calculate the squares of difference $(t_{m1} - t_{c1})^2 = (50 - 29.2)^2 = 433$. We continue in this manner for points 2, 3, and 4 to calculate the sum $s^2 = 2916$.

After calculating s^2 for $\alpha = 3$ and $k' = 5$, we make a second guess for α and k'. For our second guess we choose $\alpha = 2$ and $k' = 5$; Equation (E5-3.2) becomes

$$t_c = \frac{1}{k'}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] = \frac{1}{5}\left[\frac{1}{C_A} - 20\right] \tag{E5-3.4}$$

We now proceed with our second guess to find the sum of $(t_m - t_c)^2$ to be $s^2 = 49{,}895$, which is far worse than our first guess. So we continue to make more guesses of α and k' and find s^2. Let's stop and take a look at t_c for guesses 3 and 4.

P-5-19

We shall only use four points for this illustration.

TABLE E5-3.1. REGRESSION OF DATA

	Original Data		Guess 1		Guess 2		Guess 3		Guess 4	
			$\alpha = 3$, $k' = 5$		$\alpha = 2$, $k' = 5$		$\alpha = 2$, $k' = 0.2$		$\alpha = 2$, $k' = 0.1$	
	t (min)	$C_A \times 10^3$ (mol/dm^3)	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$
1	0	50	0	0	0	0	0	0	0	0
2	50	38	29.2	433	1.26	2,375	31.6	339	63.2	174
3	100	30.6	66.7	1,109	2.5	9,499	63.4	1,340	126.8	718
4	200	22.2	163	1,375	5.0	38,622	125.2	5,591	250	2,540
				$s^2 = 2916$		$s^2 = 49{,}895$		$s^2 = 7270$		$s^2 = 3432$

Summary Notes

We see that ($k' = 0.2$ dm^3/mol · min) underpredicts the time (e.g., 31.6 min versus 50 minutes), while ($k' = 0.1$ dm^3/mol · min) overpredicts the time (e.g., 63 min versus 50 minutes). We could continue in this manner by choosing k' between $0.1 < k' < 0.2$, but why bother to go to all the trouble? Nobody has that much time on their hands. Why don't we just let the Polymath regression program find the values of k' and α that will minimize s^2?

Polymath tutorial on regression is given on the CD-ROM.

The Polymath tutorial on the CD-ROM shows screen shots of how to enter the raw data in Table E5-1.1 and to carry out a nonlinear regression on Equation (E5-3.1). For $C_{A0} = 0.05$ mol/dm^3, that is, Equation (E5-3.1) becomes

$$t_c = \frac{1}{k'}\frac{(0.05)^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)}$$

We want to minimize the sum to give α and k'

$$s^2 = \sum_{i=1}^{N}(t_{mi} - t_{ci})^2 = \sum_{i=1}^{N}\left[t_{mi} - \frac{0.05^{1-\alpha} - C_{Ai}^{1-\alpha}}{k'(1-\alpha)}\right]^2 \qquad (5\text{-}22)$$

TABLE E5-3.2. RESULTS OF 1ST REGRESSION

POLYMATH Results
Example 5-3 Use of Regression to Find Rate Law Parameters 08-05-2004

Nonlinear regression (L-M)

Model: t = (.05^(1-a)-Ca^(1-a))/(k*(1-a))

Variable	Ini guess	Value	95% confidence
a	3	2.04472	0.0317031
k	0.1	0.1467193	0.0164118

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9999717
R^2adj = 0.999966
Rmsd = 0.2011604
Variance = 0.3965618

TABLE E5-3.3. RESULTS OF 2ND REGRESSION

POLYMATH Results
Example 5-3 Use of Regression to Find Rate Law Parameters 08-05-2004

Nonlinear regression (L-M)

Model: t = (.05^(1-2)-Ca^(1-2))/(k*(1-2))

Variable	Ini guess	Value	95% confidence
k	0.1	0.1253404	7.022E-04

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9998978
R^2adj = 0.9998978
Rmsd = 0.3821581
Variance = 1.1926993

P. 5-20

The results shown are

$\alpha = 2.04$	$\alpha = 2.0$
$k' = 0.147\ \text{dm}^3/\text{mol}\cdot\text{min}$	$k' = 0.125\ \text{dm}^3/\text{mol}\cdot\text{min}$

We shall round off α to make the reaction second order, (i.e., $\alpha = 2.00$). Now having fixed α at 2.0, we must do another regression [cf. Table E5-3.3] on k' because the k' given in Table E.5-3.1 is for $\alpha = 2.0447$. We now regress the equation

$$t = \frac{1}{k'}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$$

and find $k' = 0.125\ \text{dm}^3/\text{mol}\cdot\text{min}$.

$$k = \frac{k'}{C_{A0}} = 0.25\left(\frac{\text{dm}^3}{\text{mol}}\right)^2/\text{min}$$

We note that the reaction order is the same as that in Examples 5-1 and 5-2; however, the value of k is about 8% larger.

Model Discrimination. One can also determine which model or equation best fits the experimental data by comparing the sums of the squares for each model and then choosing the equation with a smaller sum of squares and/or carrying out an F-test. Alternatively, we can compare the residual plots for each model. These plots show the error associated with each data point, and one looks to see if the error is randomly distributed or if there is a trend in the error. When the error is randomly distributed, this is an additional indication that the correct rate law has been chosen. An example of model discrimination using nonlinear regression is given on the CD-ROM in Chapter 10 of the *Summary Notes*.

Links

5.3 Method of Initial Rates

:d when reactions are reversible

The use of the differential method of data analysis to determine reaction orders and specific reaction rates is clearly one of the easiest, since it requires only one experiment. However, other effects, such as the presence of a significant *reverse* reaction, could render the differential method ineffective. In these cases, the method of initial rates could be used to determine the reaction order and the specific rate constant. Here, a series of experiments is carried out at different initial concentrations, C_{A0}, and the initial rate of reaction, $-r_{A0}$, is determined for each run. The initial rate, $-r_{A0}$, can be found by differentiating the data and extrapolating to zero time. For example, in the Trityl–Methanol reaction shown in Example 5-1, the initial rate was found to be 0.00028 mol/dm^3 · min. By various plotting or numerical analysis techniques relating $-r_{A0}$ to C_{A0}, we can obtain the appropriate rate law. If the rate law is in the form

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

the slope of the plot of $\ln(-r_{A0})$ versus $\ln C_{A0}$ will give the reaction order α.

5.2 Method of Initial Rates

若 experimental data 準確, differential method 是決定 irrev. rxn, $A \longrightarrow$ products, kinetic parameters 的好方法。

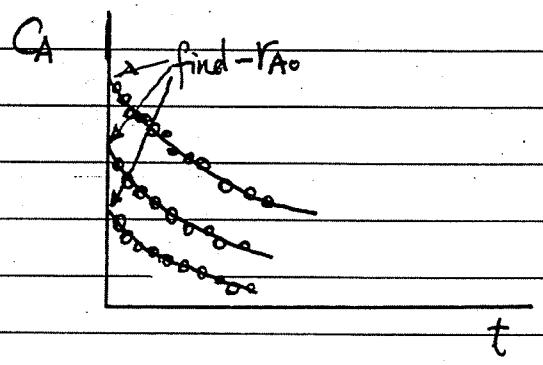
但若 reverse rxn 存在, i.e. $A \rightleftharpoons$ products, differential method 就無法求出 $A \longrightarrow$ products 的 kinetics

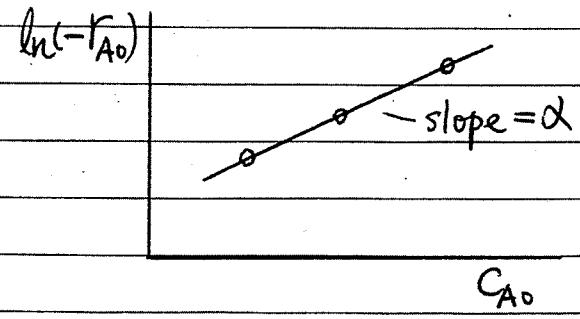
在 $t \to 0$, $C_{prod} \to 0$, $C_A = C_{A0}$

$$\therefore \quad -\frac{dC_A}{dt} = -r_{A0} = k C_{A0}^{\alpha}$$

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

experiments : const-V BR





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Example 5–3 Method of Initial Rates in Solid–Liquid Dissolution Kinetics

The dissolution of dolomite, calcium magnesium carbonate, in hydrochloric acid is a reaction of particular importance in the acid stimulation of dolomite oil reservoirs.[4] The oil is contained in pore space of the carbonate material and must flow through the small pores to reach the well bore. In matrix stimulation, HCl is injected into a well bore to dissolve the porous carbonate matrix. By dissolving the solid carbonate the pores will increase in size, and the oil and gas will be able to flow out at faster rates, thereby increasing the productivity of the well.[5] The dissolution reaction is

$$4HCl + CaMg(CO_3)_2 \rightarrow Mg^{2+} + Ca^{2+} + 4Cl^- + 2CO_2 + 2H_2O$$

The concentration of HCl at various times was determined from atomic-absorption spectrophotometer measurements of the calcium and magnesium ions.

Determine the reaction order with respect to HCl from the data presented in Figure E5-3.1 for this batch reaction. Assume that the rate law is in the form given by Equation (5-1) and that the combined rate law and mole balance for HCl can be given by Equation (5-6).

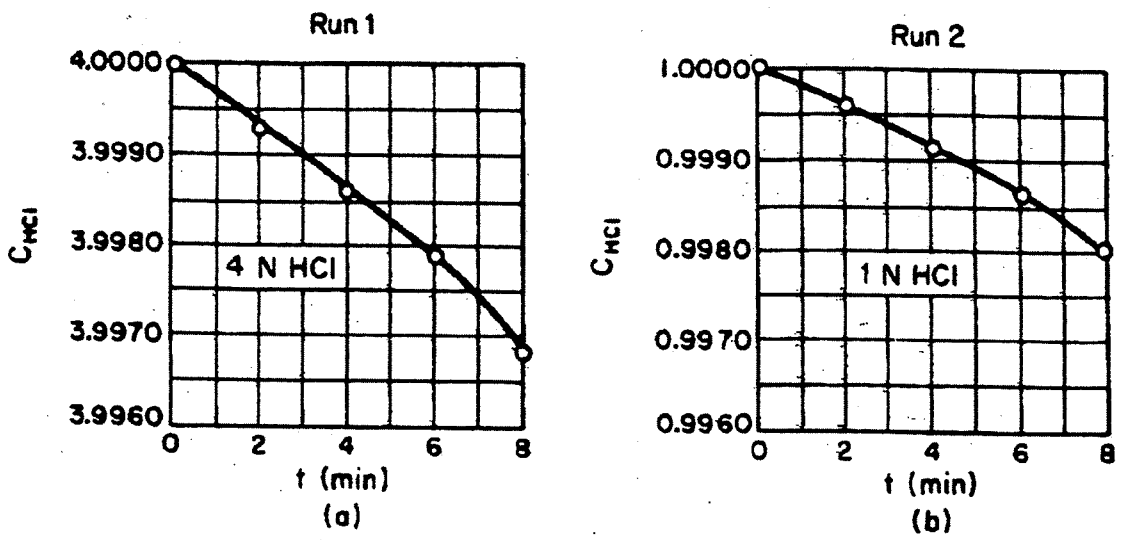

Figure E5-3.1 Concentration–time data.

Solution

Evaluating the mole balance on a constant-volume batch reactor at time $t = 0$ gives

$$\left(-\frac{dC_{HCl}}{dt}\right)_0 = -(r_{HCl})_0 = kC_{HCl,0}^{\alpha} \qquad \text{(E5-3.1)}$$

Taking the log of both sides of Equation (E5-3.1), we have

$$\ln\left(-\frac{dC_{HCl}}{dt}\right)_0 = \ln k + \alpha \ln C_{HCl,0} \qquad \text{(E5-3.2)}$$

The derivative at time $t = 0$ can be found from the slope of the plot of concentration versus time evaluated at $t = 0$. Figure E5-3.1(a) and (b) give

4 N HCl solution	1 N HCl solution
$-r_{HCl,0} = -\dfrac{3.9982 - 4.0000}{5 - 0}$	$-r_{HCl,0} = -\dfrac{0.9987 - 1.0000}{6 - 0}$
$-r_{HCl,0} = 3.6 \times 10^{-4}$ g mol/L · min	$-r_{HCl,0} = 2.2 \times 10^{-4}$ g mol/L · min

Converting to a rate per unit area, $-r''_A$, and to seconds (30 cm² of solid per liter of solution), the rates at 1 N and 4 N become 1.2×10^{-7} mol/cm²·s and 2.0×10^{-7} mol/cm²·s, respectively. We also could have used either POLYMATH or the differentiation formulas to find the derivative at $t = 0$.

If we were to continue in this manner, we would generate the following data set.[6]

TABLE 5-3.

$C_{HCl,0}$ (gmol/liter)	1.0	4.0	2.0	0.1	0.5
$-r''_{HCl,0}$ (mol/cm²·s) × 10^7	1.2	2.0	1.36	0.36	0.74

These data are plotted on Figure E5-3.2. The slope of this ln-ln plot of $-r''_{HCl,0}$ versus $C_{HCl,0}$ shown in Figure E5-3.2 gives a reaction order of 0.44. The rate law is

$$-r''_{HCl,0} = kC_{HCl}^{0.44} \qquad \text{(E5-3.3)}$$

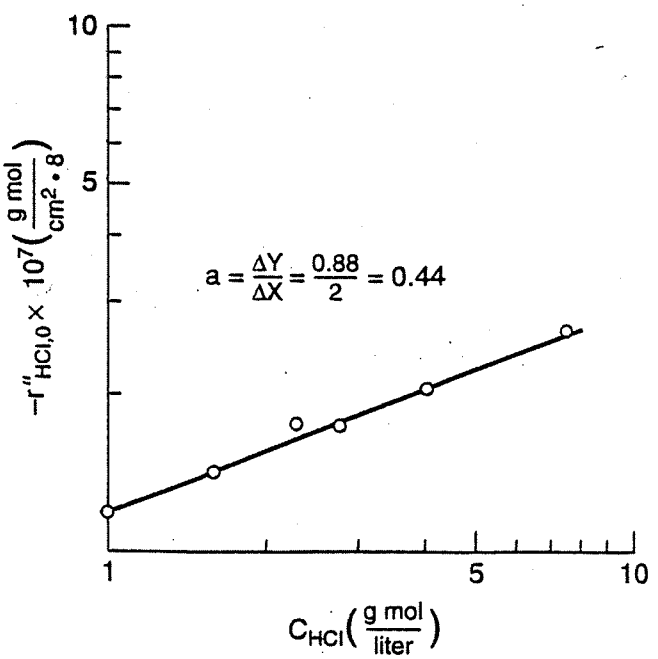

Figure E5-3.2 Initial rate as a function of initial HCl concentration.

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5-3 Method of Half-lives

$A \longrightarrow$ products (若為 $A+B \longrightarrow$ prod., 則配合 method of excess)

const-V BR

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

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

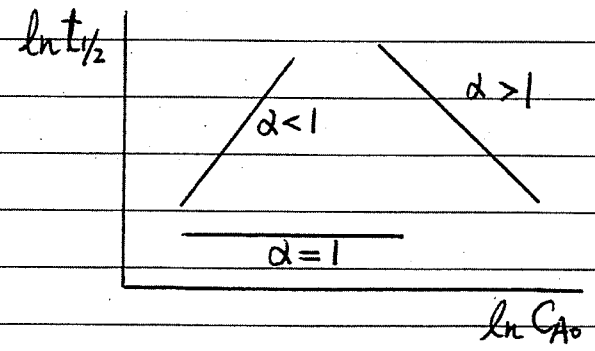
$$= \frac{1}{kC_{A0}^{\alpha-1}(\alpha-1)}\left[\left(\frac{C_{A0}}{C_A}\right)^{\alpha-1} - 1\right]$$

$C_A = \frac{1}{2}C_{A0}$ at $t = t_{1/2}$ = half-life

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

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

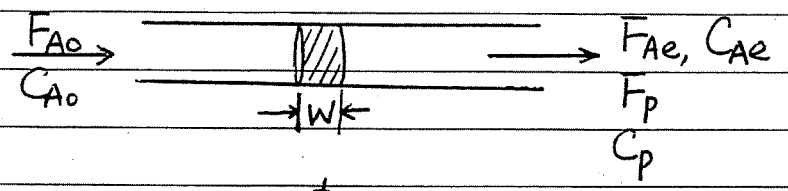
改變 C_{A0}, 求 $t_{1/2}$ $\Longrightarrow$ α 值 (from slope of $\ln t_{1/2}$ vs. $\ln C_{A0}$)



$$\ln t_{1/2} = \ln\frac{0.693}{k} \text{ for } \alpha = 1$$

5.4 Differential Reactors

definition : small conversion of reactant, 通常用於 catalytic rxns.



$$A \xrightarrow{cat.} P$$

∵ small conversion ⟹ gradientless in the reactor, i.e. isothermal

conc. in reactor ⟶ $C_{Ab} \approx \frac{1}{2}(C_{A0}+C_{Ae}) \approx C_{A0}$

$v_0 \approx v$

same rxn rate in the bed

mole balance on A

$$F_{A0} - F_{Ae} + (r_A')(W) = 0$$

$$-r_A' = \frac{F_{A0} - F_{Ae}}{W} = \frac{F_{A0}X}{W} = \frac{F_P}{W}$$

$$= \frac{v_0 C_{A0} - v C_A}{W} \approx \frac{v_0 (C_{A0} - C_{Ae})}{W} = \frac{v_0 C_P}{W}$$

$-r_A'$	$C_{Ab}(\approx C_{A0})$
⋮	⋮

⟹ kinetic parameters

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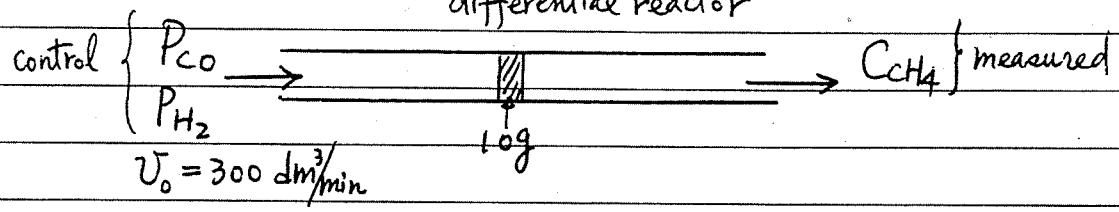
Ex. 5-4

$$3H_2 + CO \xrightarrow[\text{(Ni)}]{\text{Cat.}} CH_4 + 2H_2O$$

differential reactor



Run	P_{CO}(atm)	P_{H_2}(atm)	C_{CH_4}($gmol/dm^3$)
1	1.0	1.0	2.44×10^{-4}
2	1.8	1.0	4.40×10^{-4}
3	4.08	1.0	10.0×10^{-4}
4	1.0	0.1	1.65×10^{-4}
5	1.0	0.5	2.47×10^{-4}
6	1.0	4.0	1.75×10^{-4}

a) find $-r_A' = r'_{CH_4}$

$$-r_A' = r'_{CH_4} = \frac{F_{CH_4}}{W} = \frac{v_0 C_{CH_4}}{W}$$

Run 1 $$= 300\left(\frac{dm^3}{min}\right)\cdot\frac{2.44\times10^{-4}\left(\frac{gmol}{dm^3}\right)}{10\ g\ cat.} = 7.33\times10^{-3}\ \frac{gmol\ CH_4}{g\ cat.\ min}$$

Run	P_{CO}(atm)	P_{H_2}(atm)	$C_{CH_4}\left(\frac{gmol}{dm^3}\right)$	$r'_{CH_4}\left(\frac{gmol\ CH_4}{g\ cat.\ min}\right)$
1	1.0	1.0	2.44×10^{-4}	7.33×10^{-3}
2	1.8	1.0	4.40×10^{-4}	13.2×10^{-3}
3	4.08	1.0	10.0×10^{-4}	30.0×10^{-3}
4	1.0	0.1	1.65×10^{-4}	4.95×10^{-3}
5	1.0	0.5	2.47×10^{-4}	7.42×10^{-3}
6	1.0	4.0	1.75×10^{-4}	5.25×10^{-3}

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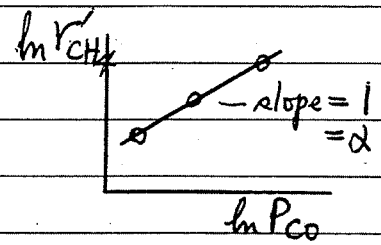
b) $r'_{CH_4} = f(CO) \cdot g(H_2)$ find rate equation

At const. P_{H_2} (runs 1, 2, 3) $\Longrightarrow$ $r'_{CH_4} \sim P_{CO}^{\alpha}$ power law

$\therefore$ rate law $\Longrightarrow$ $r'_{CH_4} = k P_{CO}^{\alpha} g(H_2)$

$= k' P_{CO}^{\alpha}$ at const. $P_{H_2} = 1$ atm

$\therefore \ln(r'_{CH_4}) = \ln k' + \alpha \ln P_{CO}$



$\therefore r'_{CH_4} = k' P_{CO}$

At const. P_{CO} (runs 1, 4, 5, 6) $\Longrightarrow$ r'_{CH_4} vs. P_{H_2} not a power law

1. at low H_2 (runs 4, 5), r'_{CH_4} increases with $P_{H_2}\uparrow$
   may be $r'_{CH_4} \sim P_{H_2}^{\beta_1}$
2. at high H_2 (runs 1, 6), r'_{CH_4} decreases with $P_{H_2}\uparrow$
   may be $r'_{CH_4} \sim 1/P_{H_2}^{\beta_2}$

Experience suggests $r'_{CH_4} \sim \dfrac{P_{H_2}^{\beta_1}}{1 + b P_{H_2}^{\beta_2}}$ (Chapter 10)

$\therefore$ at low H_2, $1 \gg b P_{H_2}^{\beta_2}$ $\Longrightarrow$ $r'_{CH_4} \sim P_{H_2}^{\beta_1}$

at hig H_2, $1 \ll b P_{H_2}^{\beta_2}$ $\Longrightarrow$ $r'_{CH_4} \sim 1/P_{H_2}^{\beta_2 - \beta_1}$, where $\beta_2 > \beta_1$

data 約略与理論 (Chapt. 10) $r'_{CH_4} = \dfrac{a P_{CO} P_{H_2}^{1/2}}{1 + b P_{H_2}}$ 符合

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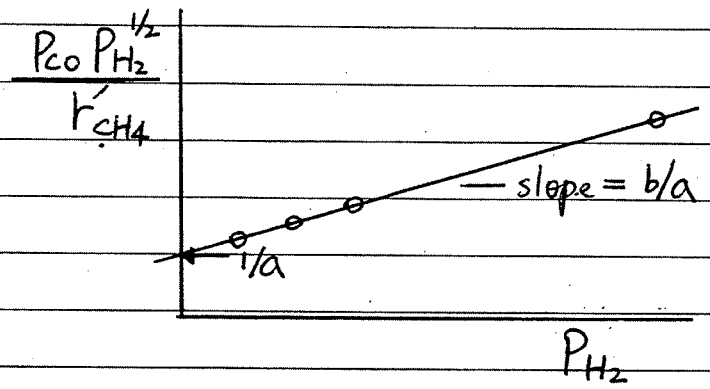
rearrange $\Rightarrow \dfrac{P_{CO} P_{H_2}^{1/2}}{r'_{CH_4}} = \dfrac{1}{a} + \dfrac{b}{a} P_{H_2}$



$$r'_{CH_4} = \frac{1.83\times10^{-2} P_{H_2}^{1/2} P_{CO}}{1 + 1.5 P_{H_2}}$$

5-5 Least-Squares Analysis

a rate law depends on the conc. of more than one species

e.g. const-V BR

$$-\frac{dC_A}{dt} = -r_A = k C_A^{\alpha} C_B^{\beta}, \quad C_A, C_B \text{ are measured}$$

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

least-squares analysis can determine the values of k, α, and β

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5-7 Laboratory Reactors

5.7.1 Integral (Fixed-Bed) Reactor

One advantage of the integral reactor is its ease of construction (see Figure 5-14). On the other hand, while channeling or bypassing of some of the catalyst by the reactant stream may not be as fatal to data interpretation in the case of this reactor as in that of the differential reactor, it may still be a problem.

Easy to construct

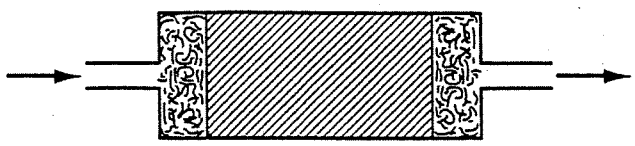


Figure 5-14 Integral reactor.

5.7.2 Stirred Batch Reactor

In the stirred batch reactor the catalyst is dispersed as a slurry, as shown in Figure 5-15. Although there will be better contacting between the catalyst and the fluid in this reactor than either the differential or integral reactors, there is a sampling problem in this reactor.

Good–fluid solid contact

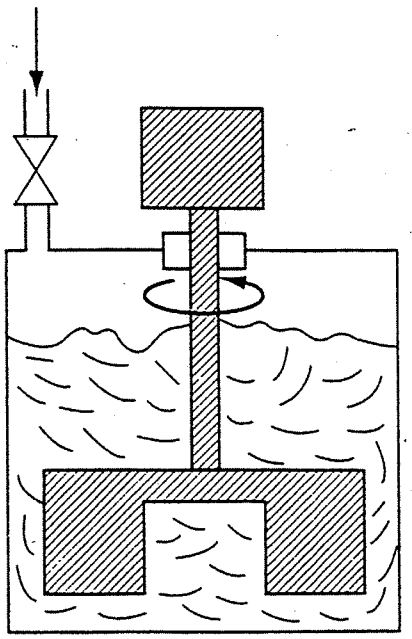


Figure 5-15 Stirred batch reactor. [From V. Weekman, *AIChE J. 20*, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

5.7.3 Stirred Contained Solids Reactor (SCSR)

Although there are a number of designs for contained solids reactors, all are essentially equivalent in terms of performance. A typical design is shown in Figure 5-16

Minimizes external mass transfer resistance

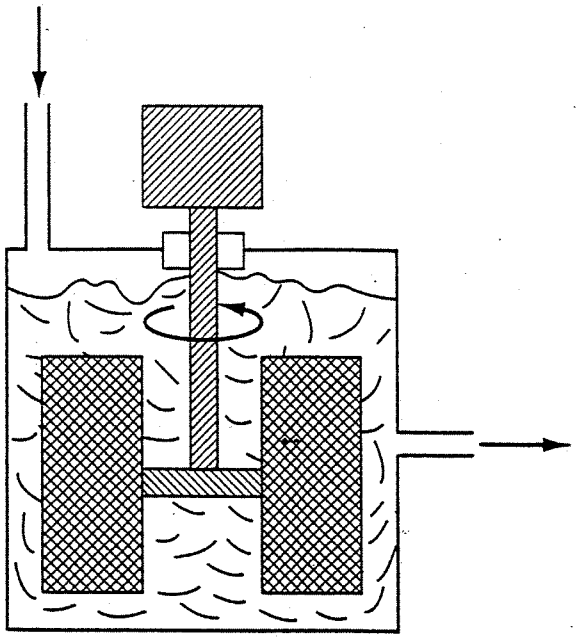


Figure 5-16 Stirred contained solids reactor. [From V. Weekman, *AIChE J. 20*, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

5.7.4 Continuous-Stirred Tank Reactor (CSTR)

The CSTR reactor (Figure 5-17) is used when there is significant catalyst decay. Fresh catalyst is fed to the reactor along with the fluid feed, and the cat-

One of the best reactors for isothermal operation

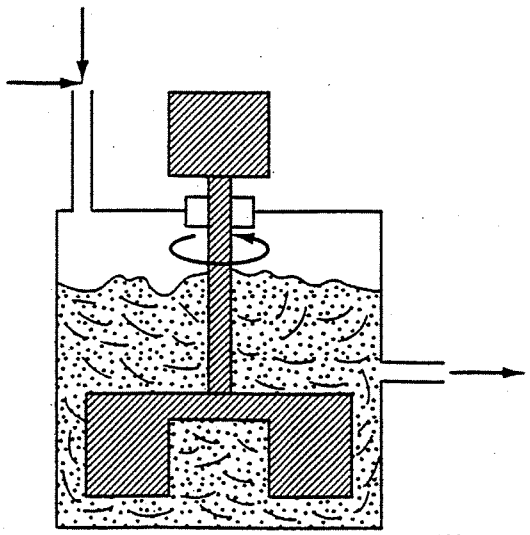


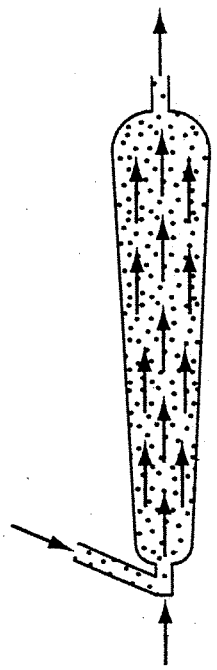
Figure 5-17 [From V. Weekman, *AIChE J. 20*, 833, (1974) with permission of the AIChE. Copyright © 1974 AIChE. All rights reserved.]

alyst leaves the reactor in the product stream at the same rate at which it is fed, to offset catalyst decay with time.

5.7.5 Straight-Through Transport Reactor

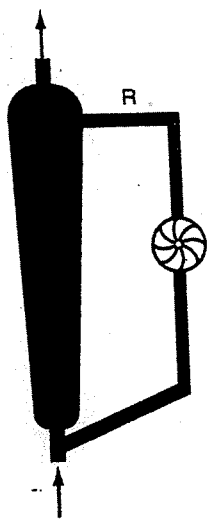
Commercially, the transport reactor (Figure 5-18) is used widely in the production of gasoline from heavier petroleum fractions. In addition, it has found use in the drying of grains. In this reactor, either an inert gas or the reactant itself transports the catalyst through the reactor.

Best for catalyst decay



5.7.6 Recirculating Transport Reactor

By recirculating the gas and catalyst through the transport reactor (Figure 5-19), one can achieve a well-mixed condition provided that the recirculation rate is large with respect to the feed rate.



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