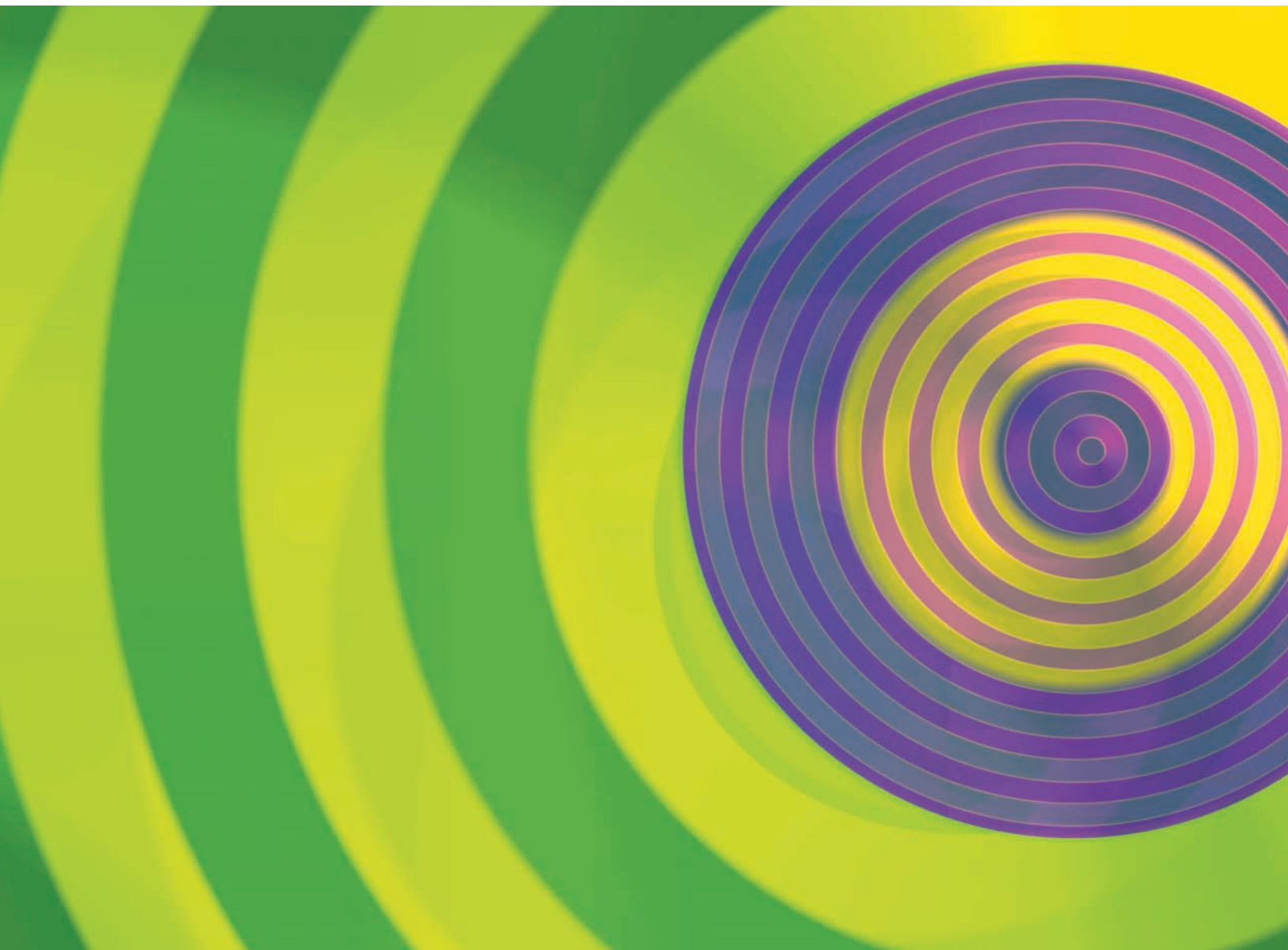


Pearson New International Edition



**Elements of Chemical Reaction
Engineering
H. Scott Fogler
Fourth Edition**

Pearson Education Limited

Edinburgh Gate

Harlow

Essex CM20 2JE

England and Associated Companies throughout the world

Visit us on the World Wide Web at: www.pearsoned.co.uk

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ISBN 10: 1-292-02616-2

ISBN 13: 978-1-292-02616-9

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

Printed in the United States of America

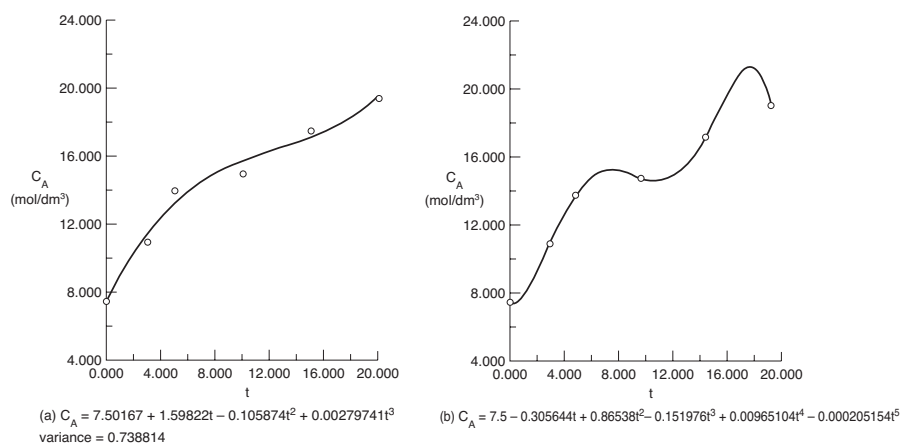


Figure 5-2 Polynomial fit of concentration–time data.

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:

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

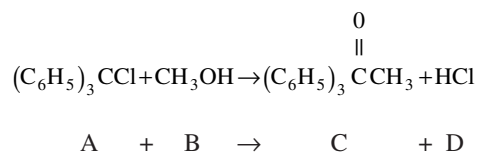
The reaction order can now be found from a plot of $\ln(-dC_A/dt)$ as a function of $\ln C_A$, as shown in Figure 5-1(a), since

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

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)



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/dm³.

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.

$$-r_A = kC_A^\alpha C_B^\beta \quad (\text{E5-1.1})$$

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

$$C_B = C_{B0} \quad (\text{E5-1.2})$$

Substituting for C_B in Equation (E5-1.1)

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

$$-r_A = k' C_A^\alpha \quad (\text{E5-1.3})$$

Step 4 Apply the CRE algorithm

Mole Balance

$$\frac{dN_A}{dt} = r_A V \quad (\text{E5-1.4})$$

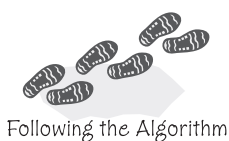
Rate Law

$$-r_A = k' C_A^\alpha \quad (\text{E5-1.3})$$

Stoichiometry: Liquid

$$V = V_0 \quad (\text{E5-1.4})$$

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



Combine: Mole balance, rate law, and stoichiometry

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

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

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

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	2.40 ^a	3.0
50	38		1.86
100	30.6	1.48	1.2
150	25.6	1.00	0.8
200	22.2	0.68	0.5
250	19.5	0.54	0.47
300	17.4	0.42	

^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.

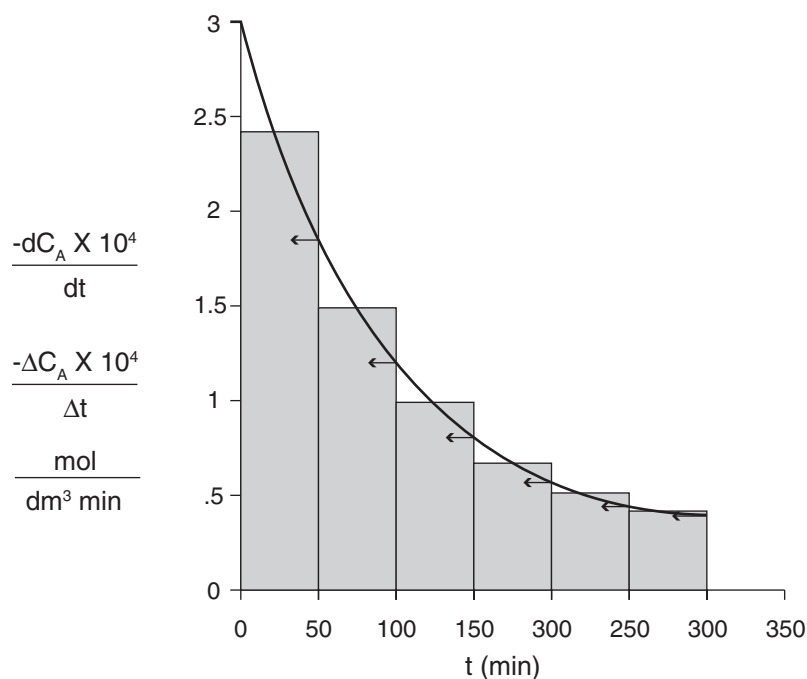


Figure E5-1.1 Graphical differentiation.

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)].

$$\begin{aligned}
 t = 0 \quad \left(\frac{dC_A}{dt} \right)_{t=0} &= \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t} \\
 &= \frac{[-3(50) + 4(38) - 30.6] \times 10^{-3}}{100} \\
 &= -2.86 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
 -\frac{dC_A}{dt} \times 10^4 &= 2.86 \text{ mol/dm}^3 \cdot \text{min}
 \end{aligned}$$

$$\begin{aligned}
 t = 50 \quad \left(\frac{dC_A}{dt} \right)_1 &= \frac{C_{A2} - C_{A0}}{2\Delta t} = \frac{(30.6 - 50) \times 10^{-3}}{100} \\
 &= -1.94 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}
 \end{aligned}$$

$$\begin{aligned}
 t = 100 \quad \left(\frac{dC_A}{dt}\right)_2 &= \frac{C_{A3} - C_{A1}}{2\Delta t} = \frac{(25.6 - 38) \times 10^{-3}}{100} \\
 &= -1.24 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
 t = 150 \quad \left(\frac{dC_A}{dt}\right)_3 &= \frac{C_{A4} - C_{A2}}{2\Delta t} = \frac{(22.2 - 30.6) \times 10^{-3}}{100} \\
 &= -0.84 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
 t = 200 \quad \left(\frac{dC_A}{dt}\right)_4 &= \frac{C_{A5} - C_{A3}}{2\Delta t} = \frac{(19.5 - 25.6) \times 10^{-3}}{100} \\
 &= -0.61 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
 t = 250 \quad \left(\frac{dC_A}{dt}\right)_5 &= \frac{C_{A6} - C_{A4}}{2\Delta t} = \frac{(17.4 - 22.2) \times 10^{-3}}{100} \\
 &= -0.48 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min} \\
 t = 300 \quad \left(\frac{dC_A}{dt}\right)_6 &= \frac{C_{A4} - 4C_{A5} + 3C_{A6}}{2\Delta t} = \frac{[22.2 - 4(19.5) + 3(17.4)] \times 10^{-3}}{100} \\
 &= -0.36 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min}
 \end{aligned}$$



Summary Notes

A Polymath tutorial for fitting data can be found on the Summary 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

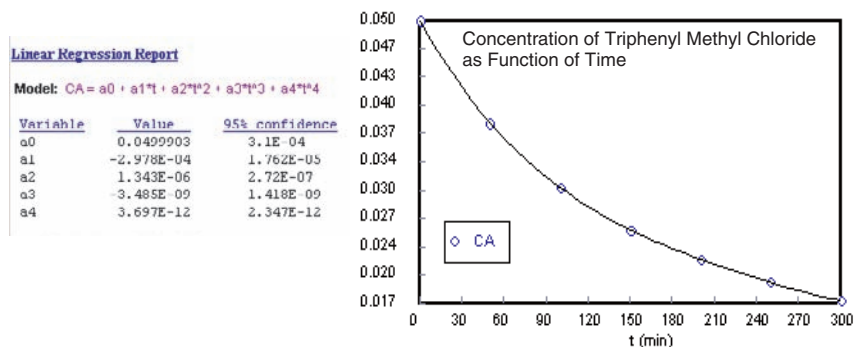


Figure E5-1.2 Polynomial fit.