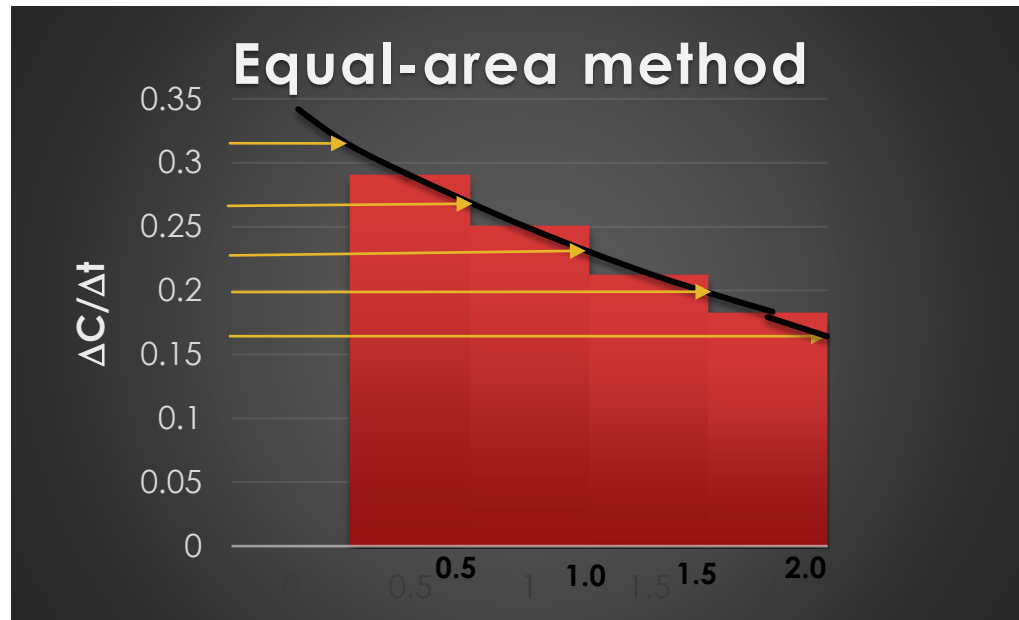


Lecture # 10.2 CHE331A

Conc vs time data to evaluate $\frac{dC_{EG}}{dt}$

time (min)	C(EG)	$\Delta(t)$	$\Delta(C)$	$\Delta C/\Delta t$	dC/dt
0	0				0.315
		0.5	0.145	0.29	
0.5	0.145				0.265
		0.5	0.125	0.25	
1	0.27				0.225
		0.5	0.106	0.212	
1.5	0.376				0.160

Graphical method



- Design and Analysis of different Reactors
- Differential method of analyzing rate data – Graphical method
- Numerical differentiation and differentiation using polynomial fits

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Numerical differentiation method can be used if data points are equally spaced

- ▶ The collection of concentration data is such that the time intervals are the same

$$t_1 - t_0 = t_2 - t_1 = \dots = \Delta t$$

- ▶ Three-point differentiation formula:

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

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

- Last point: $\left(\frac{dC_A}{dt}\right)_{t_n} = \frac{C_{A(n-2)} - 4C_{A(n-1)} + 3C_{An}}{2\Delta t}$

time (min)	C(EG)	dC/dx (Num)	dC/dx (Equal area)
0	0	0.310	0.315
0.5	0.145	0.270	0.265
1	0.27	0.231	0.225
1.5	0.376	0.193	0.200



Polynomial fit should be done with care

- ▶ The conversion versus time data is fit to an n^{th} -order polynomial:

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

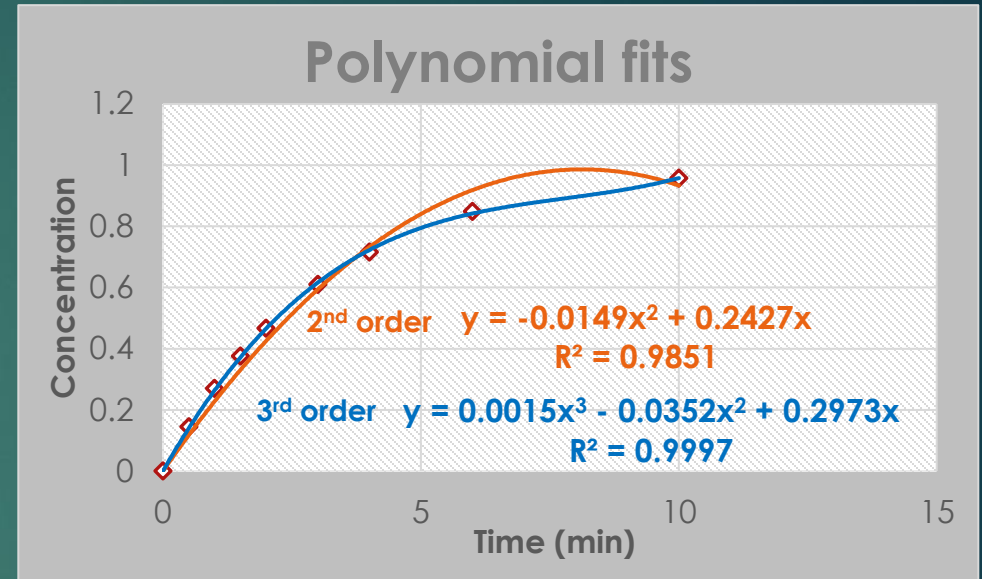
- ▶ Software packages do this readily by choosing the order of the polynomial

- Constants a_i are determined and equation is differentiated

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

- ▶ Choose the order of the polynomial with care

- Trends should be captured



time (min)	C(EG)	dC/dt (Poly)	dC/dt (Num)	dC/dt (E-A)
0	0	0.297	0.310	0.315
0.5	0.145	0.282	0.270	0.265
1	0.27	0.231	0.231	0.225
1.5	0.376	0.145	0.193	0.200



Once $\frac{dC_A}{dt}$ is determined the rate law parameters can be obtained

- ▶ For the case of $EO + H_2O \rightarrow EG$, with a rate law of $r_{EG} = -r_{EO} = k \cdot C_{EO}^\alpha C_{H_2O}^\beta$
 - With excess H_2O the rate law reduces to: $r_{EG} = k'_{EO} C_{EO}^\alpha$
- ▶ From numerical methods: $\frac{dC_{EG}}{dt}$ was obtained. Since $C_{EG} = C_{EO,0} - C_{EO}$
- ▶ $\frac{dC_{EG}}{dt} = -\frac{dC_{EO}}{dt}$ Also, with $C_{EO,0} = 1 \frac{kmol}{m^3} \Rightarrow C_{EO} = 1 - C_{EG}$
 - Then, α determined from: $\ln\left(-\frac{dC_{EO}}{dt}\right) = \ln k'_{EO} + \alpha \cdot \ln C_{EO}$
- ▶ Thus, $\alpha = 1$; knowing $-\frac{dC_{EO}}{dt}$ at specific C_{EO} , $\langle k'_{EO} \rangle = 0.313 \text{ min}^{-1}$

$$-r_A = 0.313 C_A \frac{\text{mole}}{\text{L} \cdot \text{min}}$$

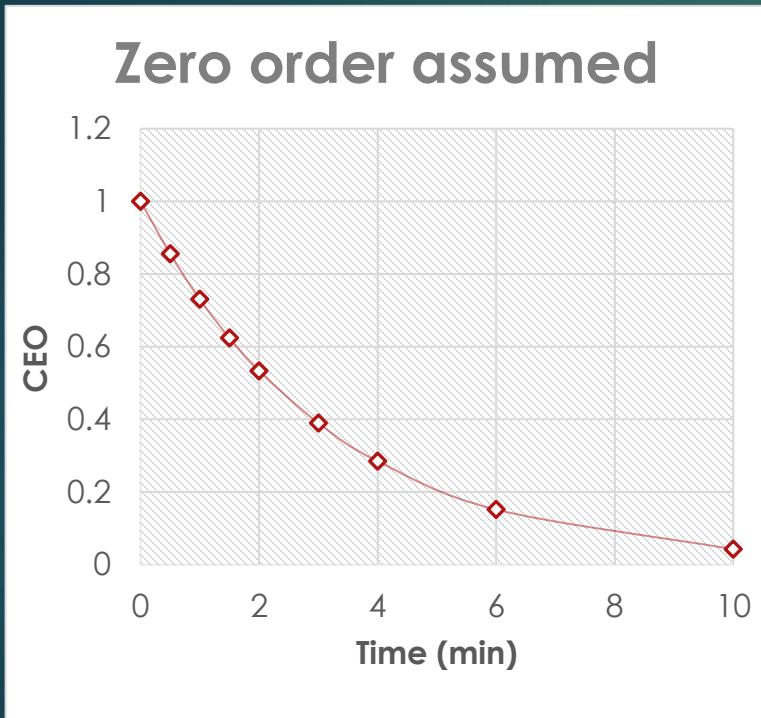


Integral method is used to determine rate constant at different temperatures

- ▶ Order is usually known or is assumed
- ▶ Mole balance equation for batch reactor is integrated to obtain the C_A vs time data, which is compared with experimental values
- ▶ $EO + H_2O \rightarrow EG$ in a constant-volume batch reactor
- ▶ Mole balance: $\frac{dC_{EG}}{dt} = r_{EG} = k'_{EO} C_{EO}^\alpha$, given $C_{EG}(t) \rightarrow C_{EO} = C_{EO,0} - C_{EG}$
 - For $\alpha = 0$ (0 order), then C_{EO} vs time is linear with slope = k'_{EO}
 - For $\alpha = 1$ (1st order), then $\ln\left(\frac{C_{EO,0}}{C_{EO}}\right)$ vs time is linear with slope = k'_{EO}
 - For $\alpha = 2$ (2nd order), then $\frac{1}{C_{EO}}$ vs time is linear with slope = k'_{EO}



Different plots can be compared to know the proper order – plots should be linear



- ▶ 1st order is a straight line. Thus, order of $\alpha = 1$
- ▶ Rate constant (from slope of 2nd plot), $k = 0.314 \text{ min}^{-1}$

