Advanced Reactor Design

Week 3

Zeroth Parameter Models for Nonideal Reactors

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For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $r_A = kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & $k=176$ $L^2/mol^2 \cdot min$ at 320K

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0
X_A	0	0.137	0.23	0.298	0.35	0.39	0.428	0.458	0.483	0.505	0.525	0.558	0.585

Alternative approach: segregation model by Polymath:

$$\bar{X}_A = \int_0^\infty X_A(t)E(t)dt$$

$$\boxed{\frac{d\bar{X}_A}{dt} = X_A(t)E(t)}$$

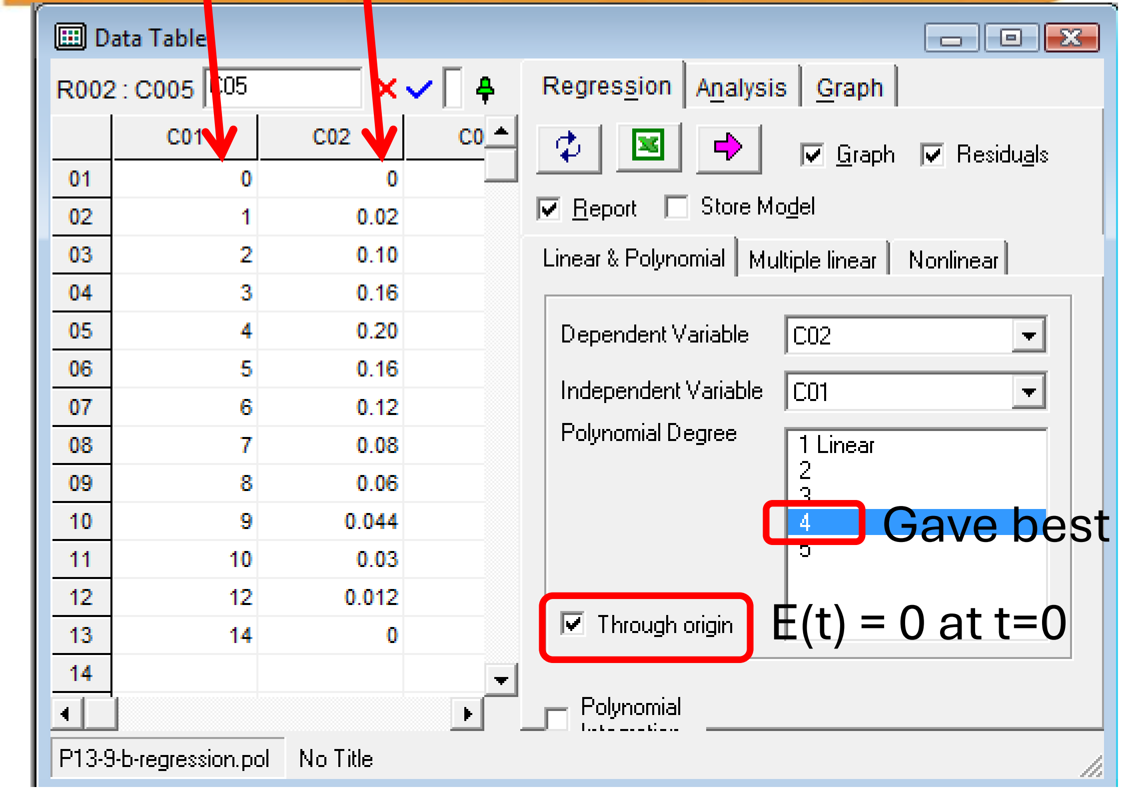
$$\boxed{X_A = 1 - \sqrt{\frac{1}{1+2kC_{B0}^2t}}}$$

↓ Need an equation for E(t)

$\boxed{k=176}$

$\boxed{C_{B0}=0.0313}$

Use Polymath to fit the E(t) vs t data in the table to a polynomial time E(t)



	C01	C02
01	0	0
02	1	0.02
03	2	0.10
04	3	0.16
05	4	0.20
06	5	0.16
07	6	0.12
08	7	0.08
09	8	0.06
10	9	0.044
11	10	0.03
12	12	0.012
13	14	0
14		

☑ Graph ☑ Residuals

☑ Report ☐ Store Model

Dependent Variable: C02

Independent Variable: C01

Polynomial Degree: 1 Linear, 2, 3, 4, 5 — 4 selected

Gave best fit

☑ Through origin

E(t) = 0 at t=0

☐ Polynomial Integration

P13-9-b-regression.pol No Title

For the irreversible, liquid-phase, nonelementary rxn $A+B \rightarrow C+D$, $-r_A = kC_AC_B^2$ Calculate the X_A using the complete segregation model using Polymath

Model: C02= a1*C01 + a2*C01^2 + a3*C01^3 + a4*C01^4

a1=0.0889237

a2= -0.0157181

a3= 0.0007926

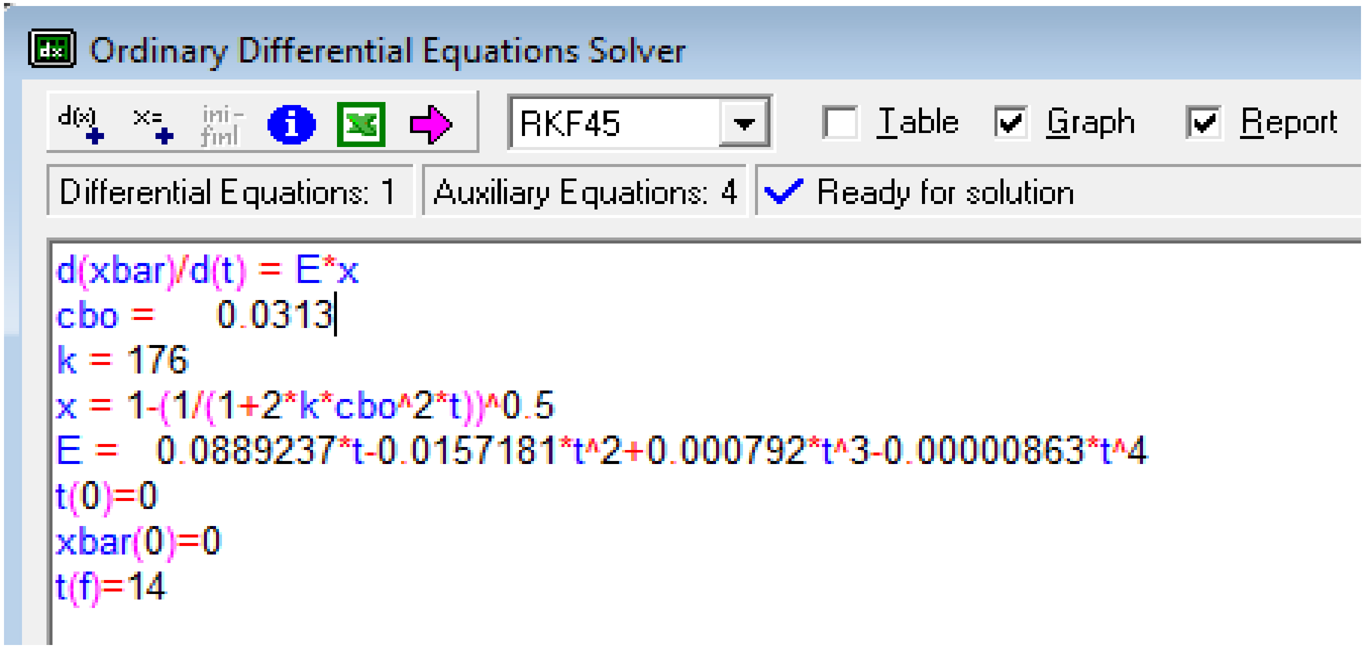
a4= -8.63E-06

Final Equation: $E = 0.0889237 t - 0.0157181 t^2 + 0.0007926 t^3 - 8.63\text{E-}6\, t^4$

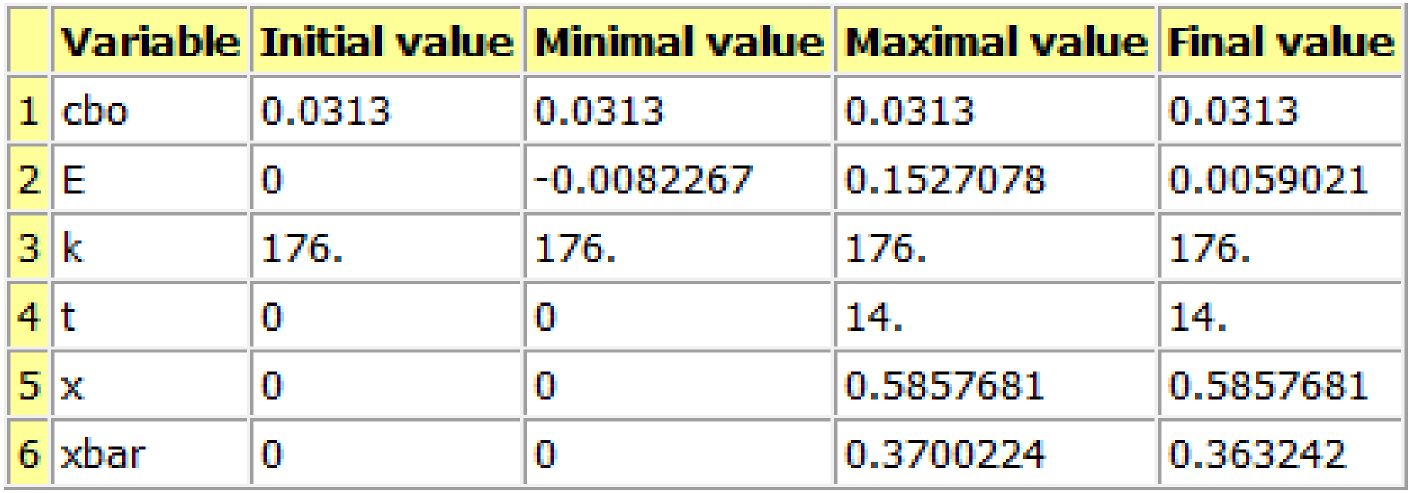
Complete segregation model by Polymath

$A+B \rightarrow C+D$

$-r_A=kC_AC_B^2$



```
d(xbar)/d(t) = E*x
cbo =      0.0313
k = 176
x = 1-(1/(1+2*k*cbo^2*t))^0.5
E =   0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
xbar(0)=0
t(f)=14
```



	Variable	Initial value	Minimal value	Maximal value	Final value
1	cbo	0.0313	0.0313	0.0313	0.0313
2	E	0	-0.0082267	0.1527078	0.0059021
3	k	176.	176.	176.	176.
4	t	0	0	14.	14.
5	x	0	0	0.5857681	0.5857681
6	xbar	0	0	0.3700224	0.363242

$\overline{X}_A = 0.36$

Segregation model by Polymath:

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & $k=176\ L^2/mol^2\cdot min$ at 320K

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Maximum mixedness model:

$$\frac{dX_A}{d\lambda}=\frac{r_A}{C_{A0}}+\frac{E(\lambda)}{1-F(\lambda)}X_A \qquad \lambda\text{=time} \qquad \frac{dF}{d\lambda}=E$$

F(λ) is a cumulative distribution function

$$\boxed{-r_A=kC_{A0}C_{B0}^2(1-X_A)^3} \qquad \boxed{C_{A0}=C_{B0}=0.0313\,mol/L} \qquad \boxed{k=176\frac{L^2}{mol^2\cdot min}}$$

Polymath cannot solve because λ→0 (needs to increase)

Substitute λ **for** z, where $z=\bar{T}-\lambda$ where $\bar{T}$=longest time interval (14 min)

$$\boxed{\frac{dX_A}{dz}=-\left(\frac{r_A}{C_{A0}}+\frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X_A\right)} \qquad \boxed{\frac{dF}{dz}=-E(\bar{T}-z)}$$

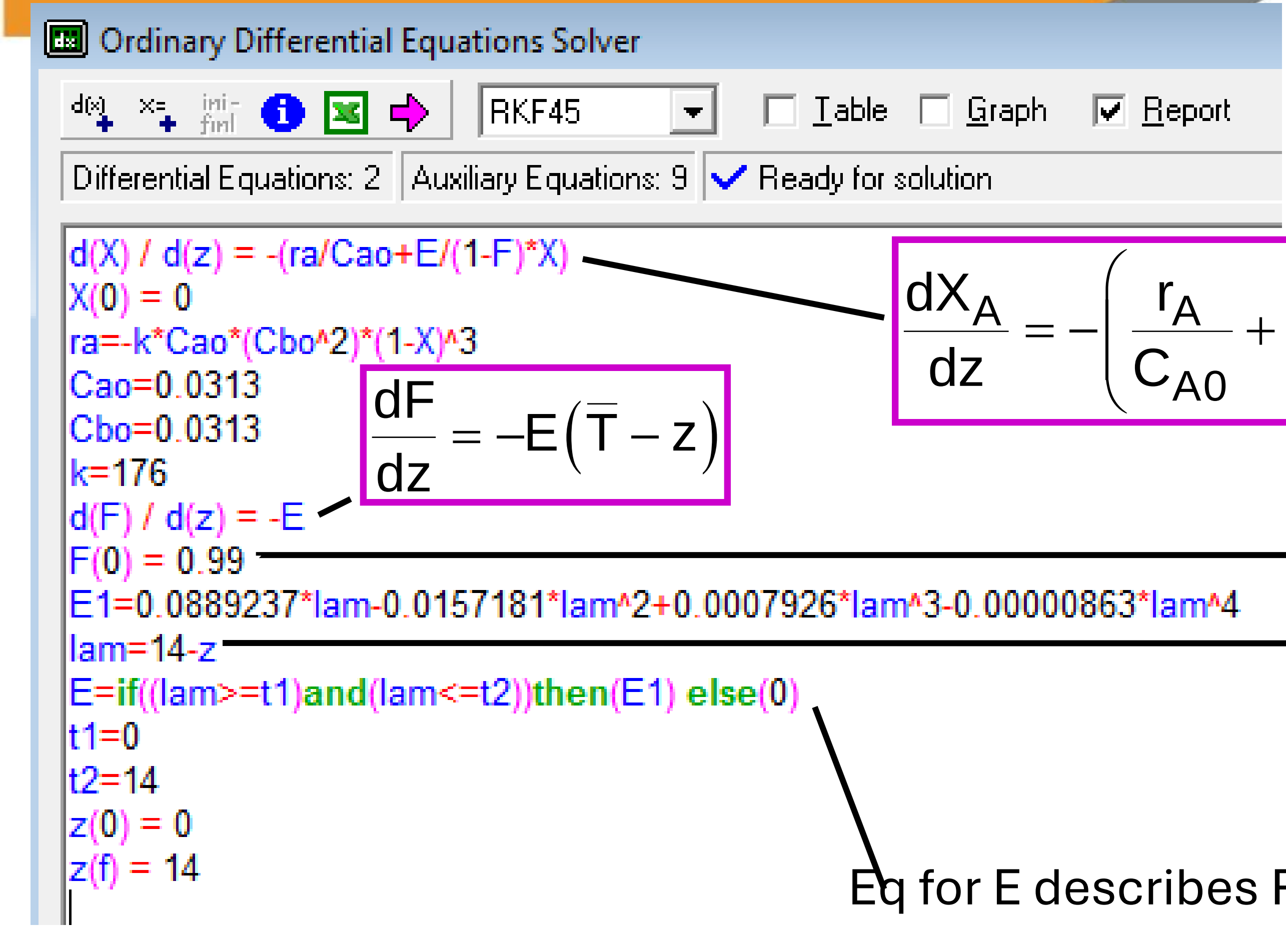
E must be in terms of $\bar{T}$-z. Since $\bar{T}$-z=λ & λ=t, simply substitute λ for t

$$\boxed{E(\lambda)=0.0889237*\lambda-0.0157181*\lambda^2+0.0007926*\lambda^3-8.63E\text{-}6*\lambda^4}$$

Maximum Mixedness Model, nonelementary reaction

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

$$-r_A = kC_AC_B^2$$



RKF45 ☐ Table ☐ Graph ☑ Report

Differential Equations: 2 Auxiliary Equations: 9 ✓ Ready for solution

```
d(X) / d(z) = -(ra/Cao+E/(1-F)*X)
X(0) = 0
ra=-k*Cao*(Cbo^2)*(1-X)^3
Cao=0.0313
Cbo=0.0313
k=176
d(F) / d(z) = -E
F(0) = 0.99
E1=0.0889237*lam-0.0157181*lam^2+0.0007926*lam^3-0.00000863*lam^4
lam=14-z
E=if((lam>=t1)and(lam<=t2))then(E1) else(0)
t1=0
t2=14
z(0) = 0
z(f) = 14
```

$$\frac{dX_A}{dz} = -\left(\frac{r_A}{C_{A0}} + \frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X_A\right)$$

$$\frac{dF}{dz} = -E(\bar{T}-z)$$

Denominator cannot = 0

$$z = \bar{T} - \lambda \rightarrow \lambda = \bar{T} - z$$

Eq for E describes RTD function only on interval t= 0 to 14 minutes, otherwise E=0

$$X_{A,\text{ maximum mixedness}} = 0.347$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A = kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with $T_0 = 288K$, $C_{A0} = C_{B0} = 0.0313$ mol/L, k=176 $L^2/mol^2 \cdot min$ at 320K, $\Delta H^\circ_{RX} = -40000$ cal/mol, E/R =3600K, $C_{PA} = C_{PB} = 20 cal/mol \cdot K$ & $C_{PC} = C_{PD} = 30 cal/mol \cdot K$

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m³	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Polymath eqs for segregation model:

$$\boxed{\frac{d\bar{X}_A}{dt} = X_A(t)E(t)} \qquad \boxed{\frac{dX_A}{dt} = kC_{B0}^2(1-X_A)^3}$$

$$\boxed{E(t) = 0.0889237*t - 0.0157181*t^2 + 0.0007926*t^3 - 8.63E\text{-}6*t^4}$$

Express k as function of T:

$$\boxed{k(T) = 176\frac{L^2}{mol^2 \cdot min}\exp\left[3600K\left(\frac{1}{320K} - \frac{1}{T}\right)\right]}$$

Need equations from energy balance. For adiabatic operation:

$$T = \frac{\left[-\Delta H^\circ_{RX}(T_R)\right]X_A + \sum_{i=1}^{n}\Theta_i C_{p_i}T_0 + X_A\Delta C_P T_R}{\left[\sum_{i=1}^{n}\Theta_i C_{p_i} + X_A\Delta C_P\right]}$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A=kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with T_0= 288K, $C_{A0}=C_{B0}$=0.0313 mol/L, k=176 $L^2/mol^2\cdot min$ at 320K, ΔH°_{RX}=-40000 cal/mol, E/R =3600K, $C_{PA}=C_{PB}$=20cal/mol·K & $C_{PC}=C_{PD}$=30 cal/mol·K

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Energy balance for adiabatic operation:

$$T=\frac{\left[-\Delta H^\circ_{RX}\left(T_R\right)\right]X_A+\sum_{i=1}^{n}\Theta_iC_{p_i}T_0+X_A\Delta C_PT_R}{\left[\sum_{i=1}^{n}\Theta_iC_{p_i}+X_A\Delta C_P\right]}$$

$$\sum_{i=1}^{n}\Theta_iC_{p_i}=C_{p_A}+C_{p_B}=40\frac{cal}{mol\cdot K}$$

Not zero!

$$\Delta C_p=\left(30+30-20-20\right)\frac{cal}{mol\cdot K}=20\frac{cal}{mol\cdot K}$$

$$\rightarrow\boxed{T=\frac{1702\frac{cal}{mol}X_A+576\frac{cal}{mol}}{2\frac{cal}{mol\cdot K}+X_A\left(\frac{cal}{mol\cdot K}\right)}}$$

$$\boxed{\frac{d\bar{X}_A}{dt}=X_A\left(t\right)E\left(t\right)}$$

$$\boxed{\frac{dX_A}{dt}=kC_{B0}^{\;2}\left(1-X_A\right)^3}$$

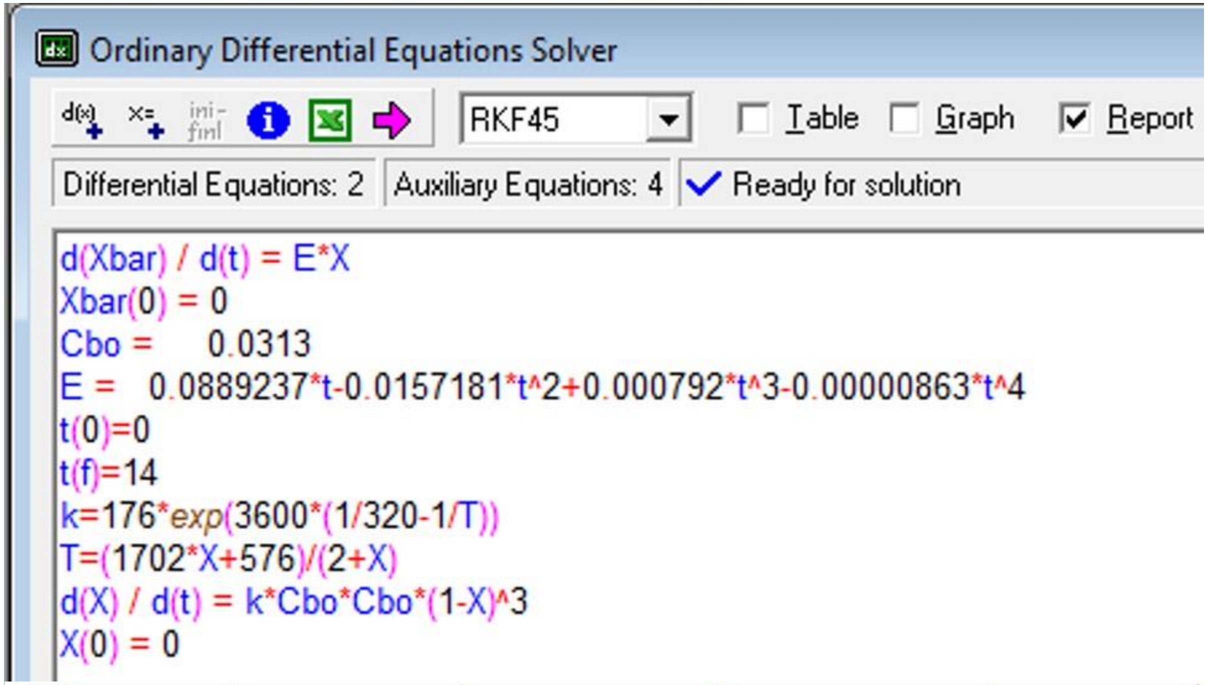
$$\boxed{k\left(T\right)=176\frac{L^2}{mol^2\cdot min}\exp\left[3600K\left(\frac{1}{320K}-\frac{1}{T}\right)\right]}$$

$$\boxed{E(t)=0.0889237*t-0.0157181*t^2+0.0007926*t^3-8.63E\text{-}6*t^4}$$

Segregation model, adiabatic operation, nonelementary reaction kinetics

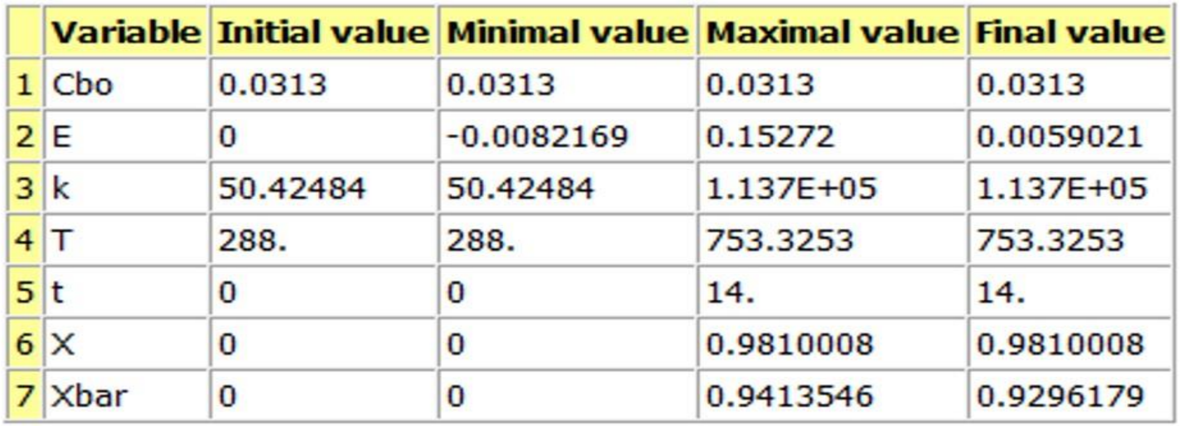
$A+B \rightarrow C+D$

$-r_A=kC_AC_B^2$



Differential Equations: 2 | Auxiliary Equations: 4 | ✓ Ready for solution

```
d(Xbar) / d(t) = E*X
Xbar(0) = 0
Cbo =     0.0313
E =  0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
t(f)=14
k=176*exp(3600*(1/320-1/T))
T=(1702*X+576)/(2+X)
d(X) / d(t) = k*Cbo*Cbo*(1-X)^3
X(0) = 0
```



	Variable	Initial value	Minimal value	Maximal value	Final value
1	Cbo	0.0313	0.0313	0.0313	0.0313
2	E	0	-0.0082169	0.15272	0.0059021
3	k	50.42484	50.42484	1.137E+05	1.137E+05
4	T	288.	288.	753.3253	753.3253
5	t	0	0	14.	14.
6	X	0	0	0.9810008	0.9810008
7	Xbar	0	0	0.9413546	0.9296179

$\bar{X}_A = 0.93$

The following slides show how the same problem would be solved and the solutions would differ if the reaction rate was still $-r_A=kC_AC_B^2$ but the reaction was instead elementary: $A+\underline{2B}\rightarrow C+D$

These slides may be provided as an extra example problem that the students may study on there own if time does not permit doing it in class.

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn A+<u>2B</u>→C+D, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model. $C_{A0}=C_{B0}=0.0313$ mol/L & k=176 $L^2/mol^2\cdot min$ at 320K

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Start with PFR design eq & see how far can we get:

$$\frac{dX_A}{dV}=\frac{-r_A}{F_{A0}}\rightarrow\frac{dX_A}{dV}=\frac{kC_AC_B^2}{C_{A0}\upsilon_0}\rightarrow\frac{dX_A}{d\tau}=\frac{kC_AC_B^2}{C_{A0}}$$

$$C_A=C_{A0}(1-X_A)\qquad \nu_b=\frac{b}{a}=\frac{2}{1}\rightarrow C_B=C_{B0}(1-2X_A)$$

$$\rightarrow\frac{dX_A}{d\tau}=\frac{k\cancel{C_{A0}}C_{B0}^2(1-X_A)(1-2X_A)^2}{\cancel{C_{A0}}}\rightarrow\boxed{\frac{dX_A}{d\tau}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

Could solve with Polymath if we knew the value of τ

$$\boxed{C_{B0}=0.0313}\qquad\boxed{k=0.0313}$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn A+2B→C+D, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

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C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0
t*E(t)	0	0.02	0.2	0.48	0.8	0.8	0.72	0.56	0.48	0.396	0.3	0.144	0

$$\boxed{\frac{dX_A}{d\tau}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

How do we determine τ?

For an ideal reactor, $\tau = t_m$

$$t_m=\int_0^\infty tE(t)dt$$

Use numerical method to determine t_m:

$$t_m=\int_0^\infty tE(t)dt=\int_0^{10} tE(t)dt+\int_{10}^{14} tE(t)dt$$

$$\int_0^{10} tE(t)dt=\frac{1}{3}\begin{bmatrix}0+4(0.02)+2(0.2)+4(0.48)+2(0.8)+4(0.8)\\ +2(0.72)+4(0.56)+2(0.48)+4(0.396)+0.3\end{bmatrix}=4.57$$

$$\int_{10}^{14} tE(t)dt=\frac{2}{3}\left[0.3+4(0.144)+0\right]=0.584$$

$$\rightarrow t_m=4.57+0.584=5.15\,\text{min}$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+\underline{2B} \rightarrow C+D$, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & $k=176\ L^2/mol^2 \cdot min$ at 320K

طريقك إلى انجاح
YOUR WAY TO SUCCESS

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0
t*E(t)	0	0.02	0.2	0.48	0.8	0.8	0.72	0.56	0.48	0.396	0.3	0.144	0

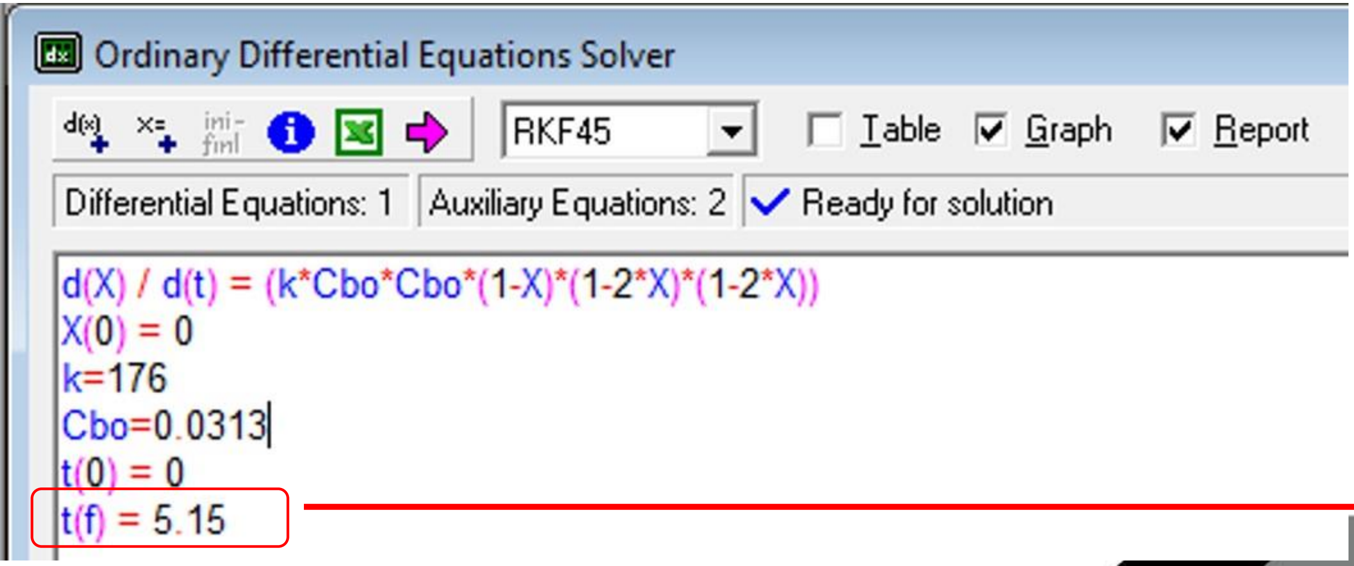
$$\boxed{\frac{dX_A}{d\tau}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

For an ideal reactor, $\tau = t_m$

$$t_m=\int_0^\infty tE(t)dt$$

$$t_m=5.15\,\text{min}=\tau$$

Final X_A corresponds to τ=5.15 min



```
d(X) / d(t) = (k*Cbo*Cbo*(1-X)*(1-2*X)*(1-2*X))
X(0) = 0
k=176
Cbo=0.0313
t(0) = 0
t(f) = 5.15
```

$$X_{A,PFR}=0.29$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn A+2B→C+D, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & k=176 $L^2/mol^2 \cdot min$ at 320K

طريقك إلى النجاح
YOUR WAY TO SUCCESS

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Segregation model with Polymath:

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt \quad \boxed{\rightarrow \frac{d\bar{X}_A}{dt}=X_A(t)E(t)}$$

$X_A(t)$ is from ***batch reactor*** design eq

Batch reactor design eq:

$$N_{A0}\frac{dX_A}{dt}=-r_AV \rightarrow \cancel{N_{A0}}\frac{dX_A}{dt}=k\cancel{C_{A0}}C_{B0}^2(1-X_A)(1-2X_A)^2\cancel{V}$$

$$N_{A0}=C_{A0}V$$

Stoichiometry:

$$\rightarrow \boxed{\frac{dX_A}{dt}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

$$C_B=C_{B0}(1-2X_A)$$

$$-r_A=kC_AC_B^2$$

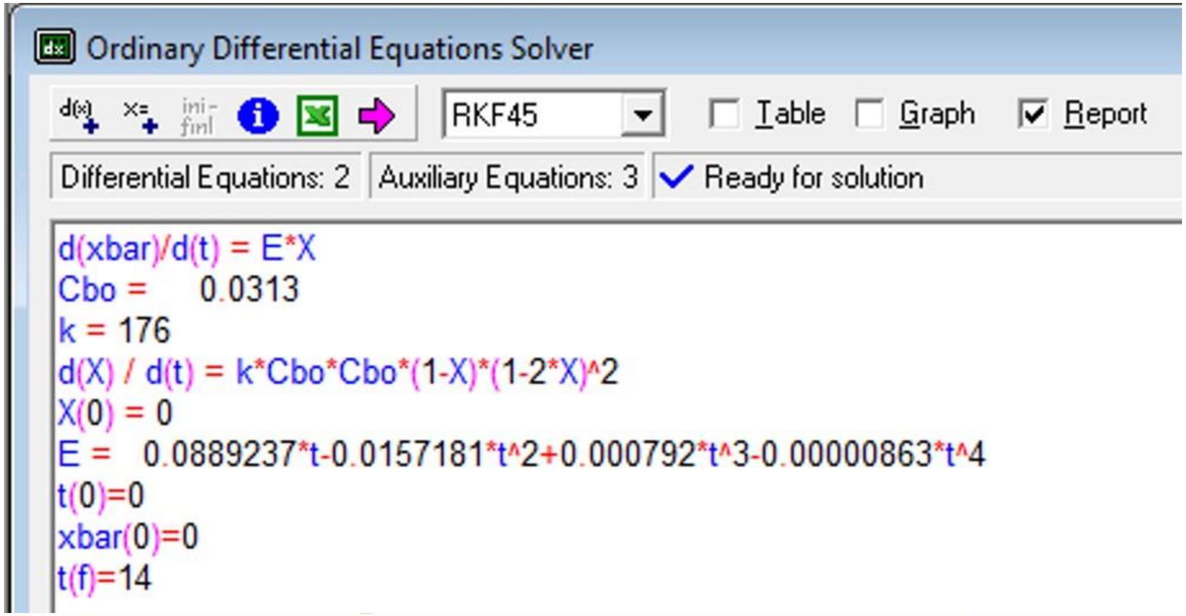
$$C_A=C_{A0}(1-X_A)$$

$\boxed{k=176}$ $\boxed{C_{B0}=0.0313}$

Best-fit polynomial line for E(t) vs t calculated by Polymath (slide 19)

$\boxed{E(t)=0.0889237*t-0.0157181*t^2+0.0007926*t^3-8.63E\text{-}6*t^4}$

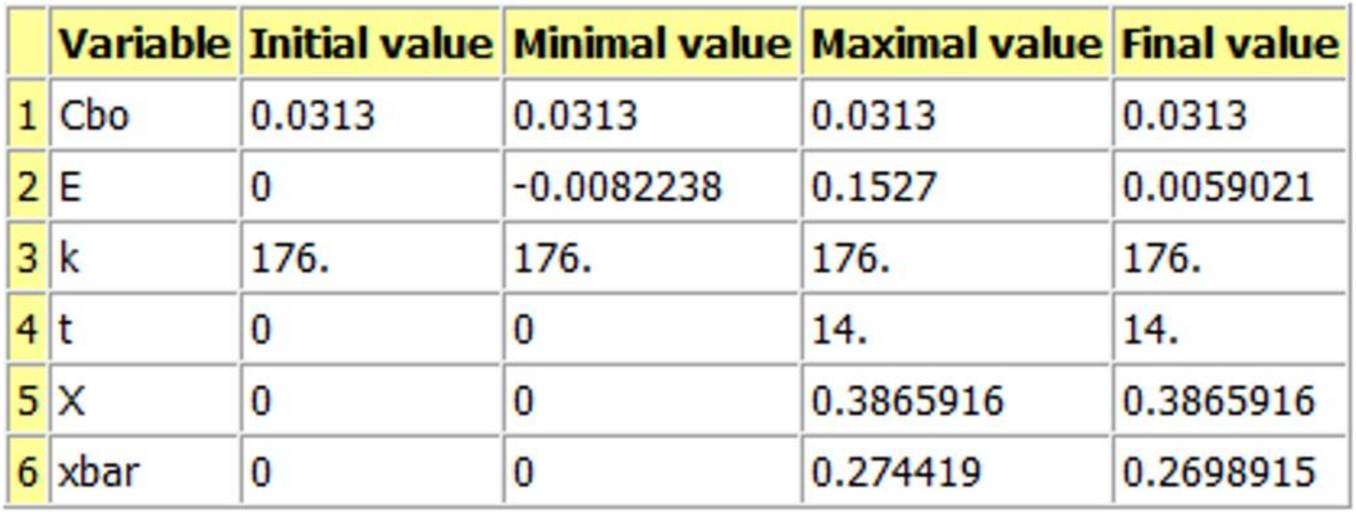
Segregation model, isothermal operation, elementary rxn: A+<u>2B</u>→C+D



RKF45 ☐ Table ☐ Graph ☑ Report

Differential Equations: 2 Auxiliary Equations: 3 ✓ Ready for solution

```
d(xbar)/d(t) = E*X
Cbo =     0.0313
k = 176
d(X) / d(t) = k*Cbo*Cbo*(1-X)*(1-2*X)^2
X(0) = 0
E =   0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
xbar(0)=0
t(f)=14
```



	Variable	Initial value	Minimal value	Maximal value	Final value
1	Cbo	0.0313	0.0313	0.0313	0.0313
2	E	0	-0.0082238	0.1527	0.0059021
3	k	176.	176.	176.	176.
4	t	0	0	14.	14.
5	X	0	0	0.3865916	0.3865916
6	xbar	0	0	0.274419	0.2698915

$$X_{A,seg} = 0.27$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+\underline{2B}\rightarrow C+D$, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

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C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Maximum mixedness model:

$$\frac{dX_A}{d\lambda}=\frac{r_A}{C_{A0}}+\frac{E(\lambda)}{1-F(\lambda)}X_A$$

λ=time

$$\frac{dF}{d\lambda}=E$$

Polymath cannot solve because λ→0 (must increase)

$$\boxed{-r_A=kC_{A0}C_{B0}^2(1-X_A)(1-2X_A)^2}$$

$$\boxed{k=176\frac{L^2}{mol^2\cdot min}}$$

$$\boxed{C_{A0}=C_{B0}=0.0313\,mol/L}$$

Substitute λ **for** z, where z=$\bar{T}$-λ where $\bar{T}$=longest time interval (14 min)

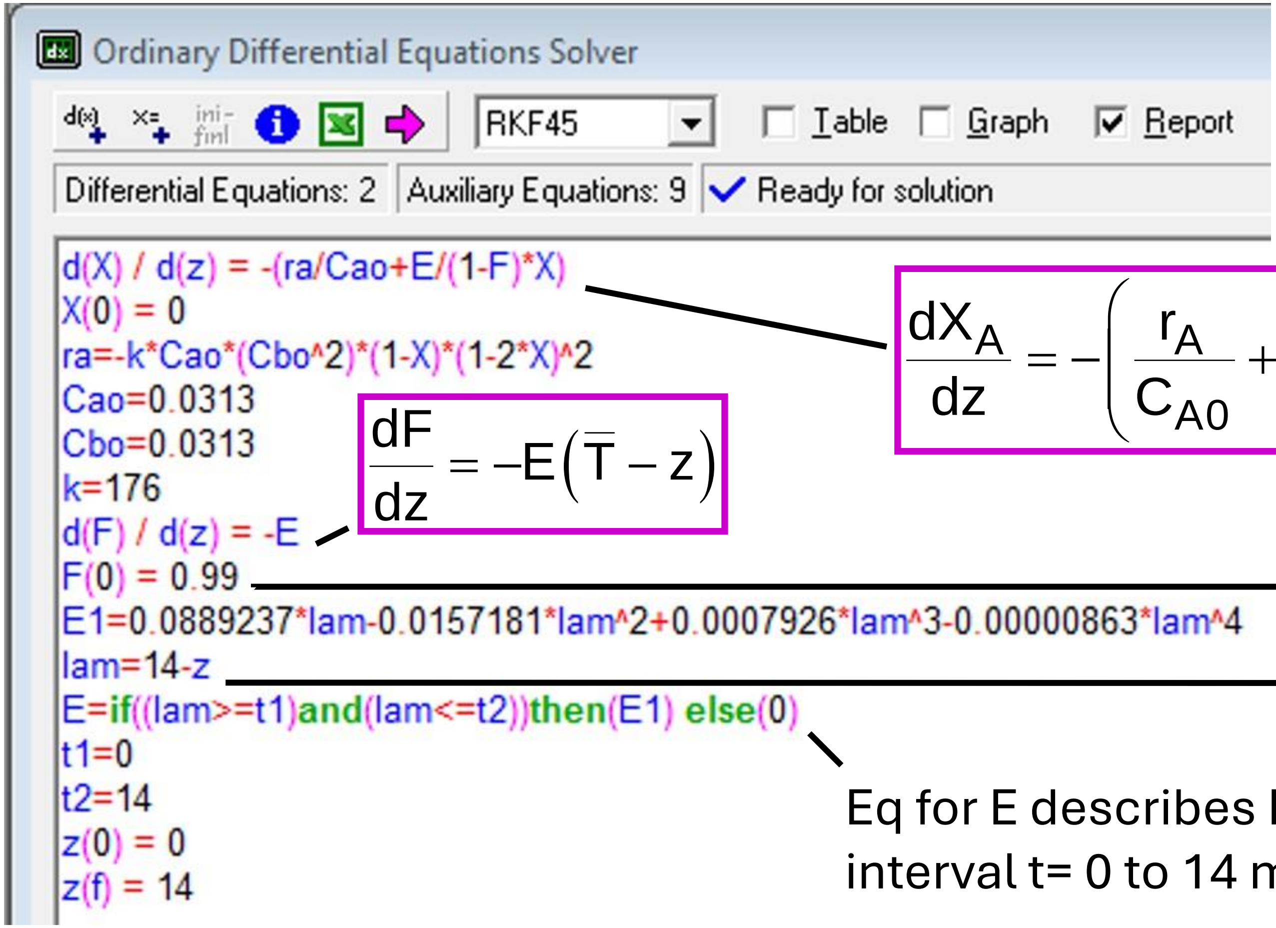
$$\boxed{\frac{dX_A}{dz}=-\left(\frac{r_A}{C_{A0}}+\frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X_A\right)}$$

$$\boxed{\frac{dF}{dz}=-E(\bar{T}-z)}$$

E must be in terms of $\bar{T}$-z. Since $\bar{T}$-z=λ & λ=t, simply substitute λ for t

$$\boxed{E(\lambda)=0.0889237*\lambda-0.0157181*\lambda^2+0.0007926*\lambda^3-8.63E\text{-}6*\lambda^4}$$

Maximum Mixedness Model, elementary reaction $A+\underline{2B}\rightarrow C+D$, $-r_A=kC_AC_B^2$



Differential Equations: 2 Auxiliary Equations: 9 ✓ Ready for solution

```
d(X) / d(z) = -(ra/Cao+E/(1-F)*X)
X(0) = 0
ra=-k*Cao*(Cbo^2)*(1-X)*(1-2*X)^2
Cao=0.0313
Cbo=0.0313
k=176
d(F) / d(z) = -E
F(0) = 0.99
E1=0.0889237*lam-0.0157181*lam^2+0.0007926*lam^3-0.00000863*lam^4
lam=14-z
E=if((lam>=t1)and(lam<=t2))then(E1) else(0)
t1=0
t2=14
z(0) = 0
z(f) = 14
```

$$\boxed{\frac{dX_A}{dz} = -\left(\frac{r_A}{C_{A0}} + \frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X_A\right)}$$

$$\boxed{\frac{dF}{dz} = -E(\bar{T}-z)}$$

Denominator cannot = 0

$$z=\bar{T}-\lambda \rightarrow \lambda=\bar{T}-z$$

Eq for E describes RTD function only on interval t= 0 to 14 minutes, otherwise E=0

$$X_{A,\text{ maximum mixedness}} = 0.25$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+\underline{2B}\rightarrow C+D$, $-r_A=kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with T_0= 288K, $C_{A0}=C_{B0}$=0.0313 mol/L, k=176 $L^2/mol^2\cdot min$ at 320K, $\Delta H°_{RX}$=-40000 cal/mol, E/R =3600K, $C_{PA}=C_{PB}$=20cal/mol·K & $C_{PC}=C_{PD}$=30 cal/mol·K

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Polymath eqs for segregation model:

$$\boxed{\frac{d\bar{X}_A}{dt}=X_A(t)E(t)}\quad \boxed{\frac{dX_A}{dt}=kC_{B0}{}^2(1-X_A)(1-2X_A)^2}$$

$$\boxed{E(t)= 0.0889237*t -0.0157181*t^2 + 0.0007926*t^3 - 8.63E\text{-}6*t^4}$$

Express k as function of T:

$$\boxed{k(T)=176\frac{L^2}{mol^2\cdot min}\exp\left[3600K\left(\frac{1}{320K}-\frac{1}{T}\right)\right]}$$

Need equations from energy balance. For adiabatic operation:

$$T=\frac{\left[-\Delta H^{\circ}_{RX}(T_R)\right]X_A+\sum_{i=1}^{n}\Theta_iC_{p_i}T_0+X_A\Delta C_PT_R}{\left[\sum_{i=1}^{n}\Theta_iC_{p_i}+X_A\Delta C_P\right]}$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+\underline{2B}\rightarrow C+D$, $-r_A=kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with $T_0=$ 288K, $C_{A0}=C_{B0}=0.0313$ mol/L, k=176 $L^2/mol^2\cdot min$ at 320K, $\Delta H^\circ_{RX}=-40000$ cal/mol, E/R =3600K, $C_{PA}=C_{PB}=20 cal/mol\cdot K$ & $C_{PC}=C_{PD}=30 cal/mol\cdot K$

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m³	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Adiabatic EB:

$$T=\frac{\left[-\Delta H^\circ_{RX}\left(T_R\right)\right]X_A+\sum_{i=1}^{n}\Theta_iC_{p_i}T_0+X_A\Delta C_PT_R}{\left[\sum_{i=1}^{n}\Theta_iC_{p_i}+X_A\Delta C_P\right]}$$

$$\Delta C_p=\left(30+30-2\left(20\right)-20\right)=0$$

$$\sum_{i=1}^{n}\Theta_iC_{p_i}=C_{p_A}+C_{p_B}=40\frac{cal}{mol\cdot K}$$

$$\boxed{T=288K+1000X_A}$$

$$\boxed{\frac{d\bar{X}_A}{dt}=X_A\left(t\right)E\left(t\right)}$$

$$\boxed{\frac{dX_A}{dt}=kC_{B0}{}^2\left(1-X_A\right)\left(1-2X_A\right)^2}$$

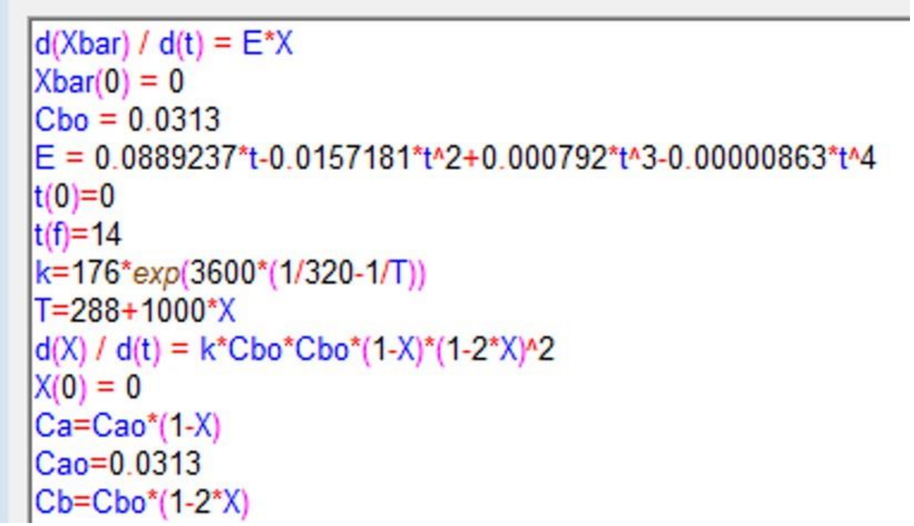
$$\boxed{k\left(T\right)=176\frac{L^2}{mol^2\cdot min}\exp\left[3600K\left(\frac{1}{320K}-\frac{1}{T}\right)\right]}$$

$E(t)= 0.0889237*t -0.0157181*t^2 + 0.0007926*t^3 - 8.63E-6*t^4$

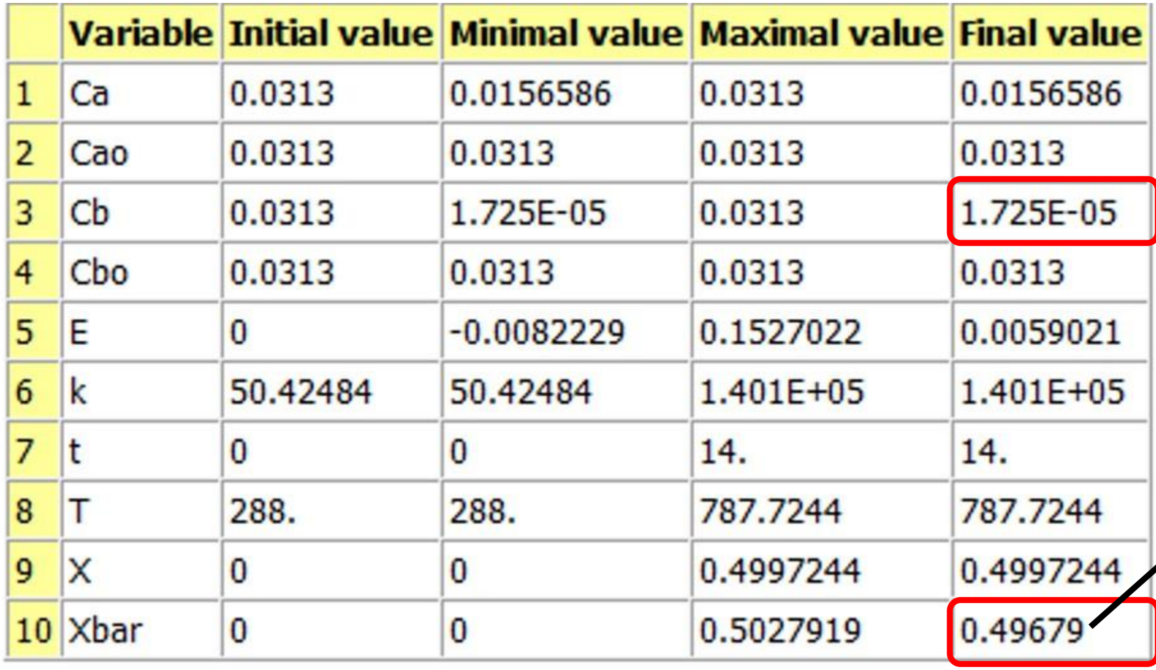
Segregation model, adiabatic operation, elementary reaction kinetics

$A+\underline{2B}\rightarrow C+D$

$-r_A=kC_AC_B^2$



```
d(Xbar) / d(t) = E*X
Xbar(0) = 0
Cbo = 0.0313
E = 0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
t(f)=14
k=176*exp(3600*(1/320-1/T))
T=288+1000*X
d(X) / d(t) = k*Cbo*Cbo*(1-X)*(1-2*X)^2
X(0) = 0
Ca=Cao*(1-X)
Cao=0.0313
Cb=Cbo*(1-2*X)
```



	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	0.0313	0.0156586	0.0313	0.0156586
2	Cao	0.0313	0.0313	0.0313	0.0313
3	Cb	0.0313	1.725E-05	0.0313	1.725E-05
4	Cbo	0.0313	0.0313	0.0313	0.0313
5	E	0	-0.0082229	0.1527022	0.0059021
6	k	50.42484	50.42484	1.401E+05	1.401E+05
7	t	0	0	14.	14.
8	T	288.	288.	787.7244	787.7244
9	X	0	0	0.4997244	0.4997244
10	Xbar	0	0	0.5027919	0.49679

Because B is completely consumed by $X_A=0.5$

$\bar{X}_A = 0.50$

Why so much lower than before?

Tanks-in-Series (T-I-S) Model

We are first going to develop the RTD equation for three tanks in series (Figure 14-2) and then generalize to n reactors in series to derive an equation that gives the number of tanks in series that best fits the RTD data.

Considering a tracer pulse injected into the first reactor of three equally sized CSTRs in series

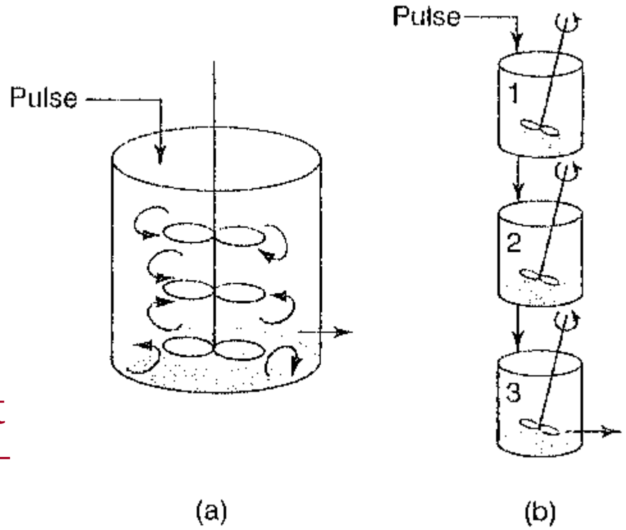


Figure 14-2 Tanks in series: (a) real system, (b) model system.

$$v = v_0$$

$$V_1 = V_2 = V_i$$

$$\tau_1 = \tau_2 = \tau_i$$

$$\tau_i = \tau / n$$

$$V_1 \frac{dC_1}{dt} = -vC_1 \longrightarrow C_1 = C_0 e^{-vt/V_1} = C_0 e^{-t/\tau_1}$$

$$C_0 = N_0 / V_1 = \frac{v_0 \int_0^\infty C_3(t)dt}{V_1}$$

$$V_i \frac{dC_2}{dt} = vC_1 - vC_2 \longrightarrow \frac{dC_2}{dt} + \frac{C_2}{\tau_i} = \frac{C_0}{\tau_i} e^{-t/\tau_i} \longrightarrow C_2 = \frac{C_0 t}{\tau_i} e^{-t/\tau_i} \longrightarrow C_3 = \frac{C_0 t^2}{2\tau_i^2} e^{-t/\tau_i}$$

$$\longrightarrow E(t) = \frac{C_3(t)}{\int_0^\infty C_3(t)dt} = \frac{C_0 t^2 /(2\tau_i^2) e^{-t/\tau_i}}{\int_0^\infty \frac{C_0 t^2 e^{-t/\tau_i}}{2\tau_i^2} dt} = \frac{t^2}{2\tau_i^3} e^{-t/\tau_i} \longrightarrow E(t) = \frac{t^{n-1}}{(n-1)!\,\tau_i^n} e^{-t/\tau_i}$$

$$\tau_i = \tau / n \longrightarrow E(\Theta) = \tau E(t) = \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta}$$

n→∞, the behavior of the system approaches that of a plug-flow reactor

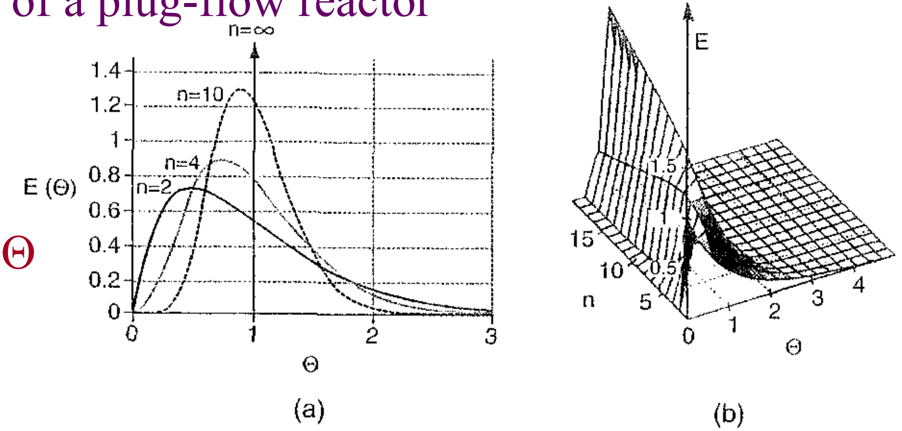


Figure 14-3 Tanks-in-series response to a pulse tracer input for different numbers of tanks.

$$\sigma_\Theta^2 = \frac{\sigma^2}{\tau^2} = \int_0^\infty (\Theta - 1)^2 E(\Theta) d\Theta$$

$$\cdots = \int_0^\infty \Theta^2 E(\Theta) d\Theta - 2\int_0^\infty \Theta E(\Theta) d\Theta + \int_0^\infty E(\Theta) d\Theta$$

$$\cdots = \int_0^\infty \Theta^2 E(\Theta) d\Theta - 1$$

$$\sigma_\Theta^2 = \int_0^\infty \Theta^2 E(\Theta) d\Theta - 1$$

$$\cdots = \int_0^\infty \Theta^2 \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta} d\Theta - 1$$

$$\cdots = \frac{n^n}{(n-1)!} \int_0^\infty \Theta^{n+1} e^{-n\Theta} d\Theta - 1$$

$$\cdots = \frac{n^n}{(n-1)!} \left[\frac{(n+1)!}{n^{n+2}} \right] - 1 = \frac{1}{n}$$

$$\int_0^\infty E(\Theta) d\Theta = 1$$

$$\int_0^\infty \Theta E(\Theta) d\Theta = 1$$

$$\longrightarrow n = \frac{1}{\sigma_\Theta^2} = \frac{\tau^2}{\sigma^2}$$

For a first order reaction,

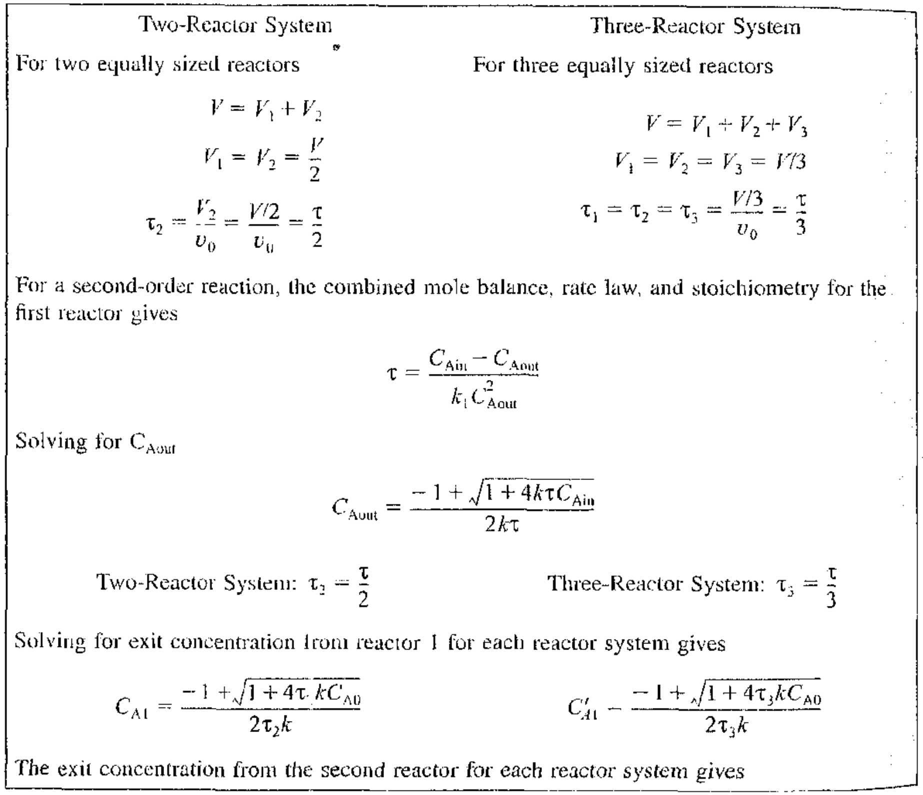
$$X = 1 - \frac{1}{(1+\tau_i k)^n} \qquad \tau_i = \frac{V}{v_0 n}$$

n may be a noninteger.

For reactions other than first order,

an integer number of reactors must be used.

TABLE 14-2. TANKS-IN-SERIES SECOND-ORDER REACTION



Two-Reactor System	Three-Reactor System
For two equally sized reactors	For three equally sized reactors
$V = V_1 + V_2$	$V = V_1 + V_2 + V_3$
$V_1 = V_2 = \frac{V}{2}$	$V_1 = V_2 = V_3 = V/3$
$\tau_2 = \frac{V_2}{v_0} = \frac{V/2}{v_0} = \frac{\tau}{2}$	$\tau_1 = \tau_2 = \tau_3 = \frac{V/3}{v_0} = \frac{\tau}{3}$

For a second-order reaction, the combined mole balance, rate law, and stoichiometry for the first reactor gives

$$\tau = \frac{C_{\text{Ain}} - C_{\text{Aout}}}{k_1 C_{\text{Aout}}^2}$$

Solving for C_{Aout}

$$C_{\text{Aout}} = \frac{-1 + \sqrt{1 + 4k\tau C_{\text{Ain}}}}{2k\tau}$$

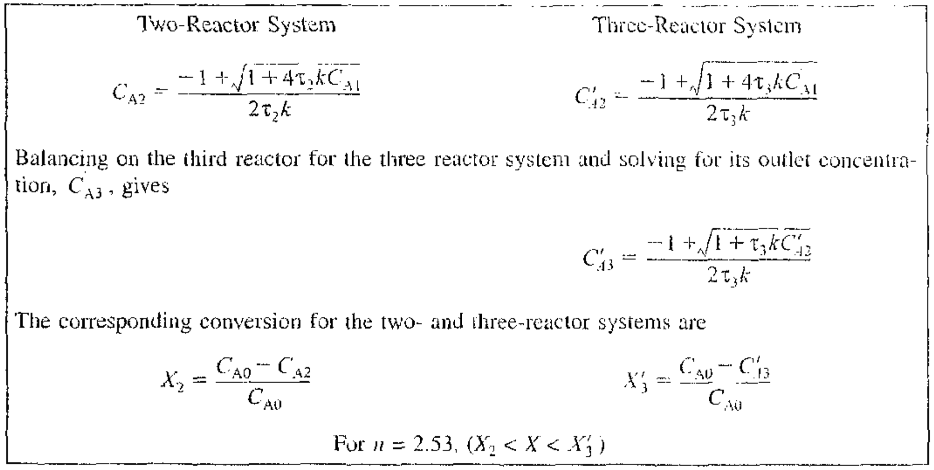
Two-Reactor System: $\tau_2 = \frac{\tau}{2}$ Three-Reactor System: $\tau_3 = \frac{\tau}{3}$

Solving for exit concentration from reactor 1 for each reactor system gives

$$C_{A1} = \frac{-1 + \sqrt{1 + 4\tau_2 kC_{A0}}}{2\tau_2 k} \qquad C'_{A1} = \frac{-1 + \sqrt{1 + 4\tau_3 kC_{A0}}}{2\tau_3 k}$$

The exit concentration from the second reactor for each reactor system gives

TABLE 14-2. TANKS-IN-SERIES SECOND-ORDER REACTION (CONTINUED)



Two-Reactor System	Three-Reactor System
$C_{A2} = \frac{-1 + \sqrt{1 + 4\tau_2 kC_{A1}}}{2\tau_2 k}$	$C'_{A2} = \frac{-1 + \sqrt{1 + 4\tau_3 kC'_{A1}}}{2\tau_3 k}$

Balancing on the third reactor for the three reactor system and solving for its outlet concentration, C'_{A3}, gives

$$C'_{A3} = \frac{-1 + \sqrt{1 + \tau_3 kC'_{A2}}}{2\tau_3 k}$$

The corresponding conversion for the two- and three-reactor systems are

$$X_2 = \frac{C_{A0} - C_{A2}}{C_{A0}} \qquad X'_3 = \frac{C_{A0} - C'_{A3}}{C_{A0}}$$

For $n = 2.53$, $(X_2 < X < X'_3)$

Example 3-1

Show that $X_{T\text{-}I\text{-}S}=X_{MM}$ for a first-order reaction

$$A \xrightarrow{k} B$$

Solution

For a first-order reaction,

$$X_{seg} = X_{MM}$$

Therefore we only need to show $X_{seg}=X_{T\text{-}I\text{-}S}$.

For a first-order reaction in a batch reactor the conversion is

$$X = 1 - e^{-kt}$$

Segregation model

$$\overline{X} = \int_0^\infty X(t)E(t)dt = \int_0^\infty (1-e^{-kt})E(t)dt = 1-\int_0^\infty e^{-kt}E(t)dt$$

$$\xrightarrow{e^{-kt} = 1-kt+\frac{k^2t^2}{2}+\text{error}} \overline{X} = \int_0^\infty \left(kt-\frac{k^2t^2}{2}\right)E(t)dt = k\int_0^\infty tE(t)dt - \frac{k^2}{2}\int_0^\infty t^2E(t)dt$$

$$\longrightarrow \quad \overline{X} = k\tau - \frac{k^2}{2}\int_0^\infty t^2 E(t)dt$$

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt$$

$$\bullet\bullet\bullet \quad = \int_0^\infty t^2 E(t)dt - 2\tau\int_0^\infty tE(t)dt + \tau^2\int_0^\infty E(t)dt \quad \longrightarrow \quad \int_0^\infty t^2 E(t)dt = \sigma^2 + \tau^2$$

$$\bullet\bullet\bullet \quad = \int_0^\infty t^2 E(t)dt - 2\tau^2 + \tau^2$$

$$\bullet\bullet\bullet \quad = \int_0^\infty t^2 E(t)dt - \tau^2 \quad \longrightarrow \quad \overline{X} = k\tau - \frac{k^2}{2}(\sigma^2 + \tau^2)$$

Tanks in Series

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n}k\right)^n} \quad \longrightarrow \quad X = 1 - \left(1 + \frac{\tau}{n}k\right)^{-n}$$

$$\bullet\bullet\bullet \quad = 1 - \left(1 - n\frac{\tau}{n}k + \frac{n(n+1)}{2}\frac{\tau^2 k^2}{n^2} + \text{error}\right)$$

$$\bullet\bullet\bullet \quad = k\tau - \frac{\tau^2 k^2}{2} - \frac{\tau^2 k^2}{2n} = k\tau - \frac{k^2}{2}\left(\tau^2 + \frac{\tau^2}{n}\right)$$

$$\xrightarrow{\sigma^2 = \frac{\tau^2}{n}} \quad X = k\tau - \frac{k^2}{2}(\tau^2 + \sigma^2) \quad \longrightarrow \quad X_{T-I-S} = X_{seg} = X_{MM}$$

Dispersion Model

In addition to transport by bulk flow, UA_cC, every component in the mixture is transported through any cross section of the reactor at a rate equal to $[-D_aA_c(dC/dz)]$ resulting from molecular and convective diffusion.

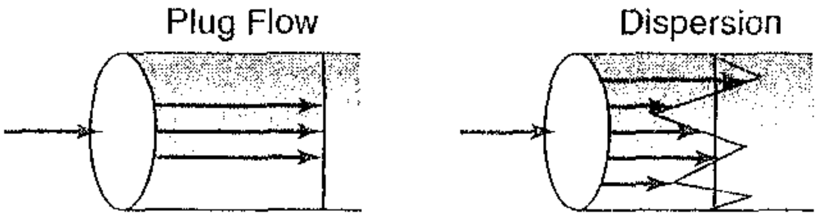


Figure 14-4 Concentration profiles (a) without and (b) with dispersion.

By convective diffusion (i.e, dispersion) we mean either Aris-Taylor dispersion in laminar flow reactors or turbulent diffusion resulting from turbulent eddies.

Radial concentration profiles for plug flow (a) and a representative axial and radial profile for dispersive flow (b) are shown in Figure 14-1.

Some molecules will diffuse forward ahead of molar average velocity while others will lag behind.

Figure 14-5 presents how dispersion causes the pulse to broaden as it moves down the reactor and becomes less concentrated.

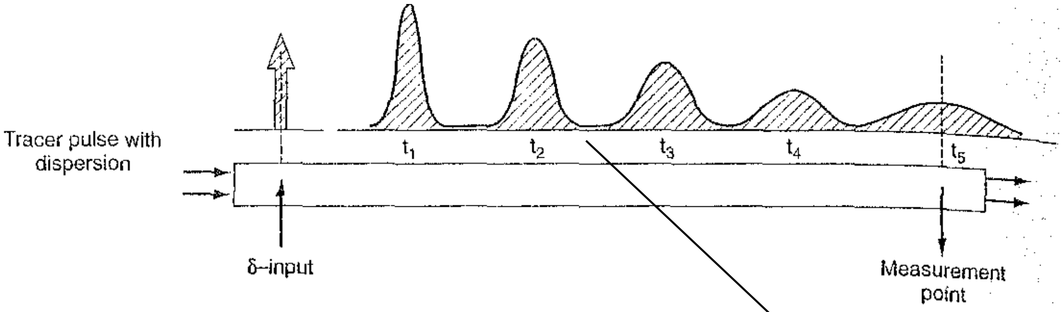


Figure 14-5 Dispersion in a tubular reactor. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

The molar flow rate of tracer (F_T) by both convection and dispersion is

$$F_T = \left(-D_a \frac{\partial C_T}{\partial z} + UC_T \right) A_c$$

D_a is the effective dispersion coefficient (m^2/s)

U is the superficial velocity (m/s)

There is a concentration gradient on both sides of the peak causing molecules to diffuse away from the peak and thus broaden the pulse. The pulse broadens as it moves through the reactor.

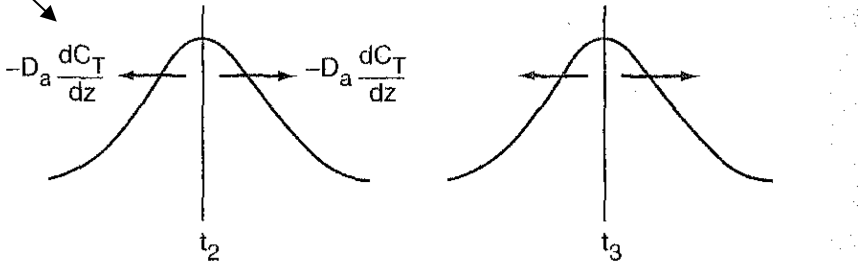


Figure 14-6 Symetric concentration gradients causing the spreading by dispersion of a pulse input.

A mole balance on the inert tracer T gives

$$-\frac{\partial F_T}{\partial z} = A_c \frac{\partial C_T}{\partial t} \longrightarrow D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (UC_T)}{\partial z} = \frac{\partial C_T}{\partial t} \longrightarrow C_T \text{ vs. } t$$

Flow, Reaction, and Dispersion

Balance Equations

A mole balance is taken on a particular component of the mixture (say, species A) over a short length Δz of a tubular reactor of cross section A_c, to arrive at

$$\left.\begin{aligned} -\frac{1}{A_c}\frac{dF_A}{dz} + r_A &= 0 \\ \frac{F_A}{A_c} &= -D_a\frac{dC_A}{dz} + UC_A \end{aligned}\right\} \longrightarrow \frac{D_a}{U}\frac{d^2C_A}{dz^2} - \frac{dC_A}{dz} + \frac{r_A}{U} = 0$$

A second-order ordinary differential equation.

Nonlinear when r_A is other than zero or fist order.

$$\xrightarrow{r_A = -kC_A} \frac{D_a}{U}\frac{d^2C_A}{dz^2} - \frac{dC_A}{dz} + \frac{-kC_A}{U} = 0 \xrightarrow{\psi = \frac{C_A}{C_{A0}},\ \lambda = \frac{z}{l}} \frac{1}{Pe_r}\frac{d^2\psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - Da\cdot\psi = 0$$

Da:Damkohler number
Pe:Peclet number

$$Da = \frac{\text{Rate of consumption of A by reaction}}{\text{Rate of transport of A by convection}} = k\tau$$

l is the characteristic length

$$Pe = \frac{\text{Rate of transport by convection}}{\text{Rate of transport by diffusion or dispersion}} = \frac{Ul}{D_a}$$

$$Pe_r = \frac{UL}{D_a}$$ reactor Peclet number

$$Pe_f = \frac{Ud_p}{\phi D_a} \text{ (for packed bed)}, \; \frac{Ud_t}{D_a} \text{ (for empty tube)}$$ fluid Peclet number

For open tubes	For packed beds
$Pe_r \sim 10^6$, $Pe_f \sim 10^4$	$Pe_r \sim 10^3$, $Pe_f \sim 10^1$

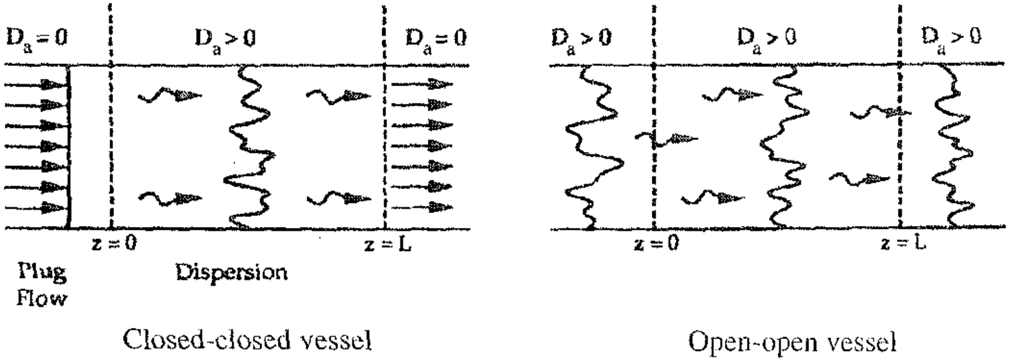
Boundary Conditions

closed-closed vessel

there is no dispersion or radial variation in concentration either upstream (closed) or downstream (closed) of the reaction section

open-open vessel

dispersion occurs both upstream (open) and downstream (open) of the reaction section



Closed-closed vessel

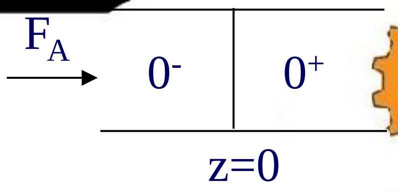
Open-open vessel

Figure 14-7 Types of boundary conditions.

A closed-open vessel boundary condition is one in which there is no dispersion in the entrance section but there is dispersion in the reaction and exit section.

Closed-Closed Vessel Boundary Condition

Danckwerts boundary conditions



At z=0

$$\left.\begin{aligned} F_A(0^-) &= F_A(0^+) \\ F_A &= -A_c D_a \frac{\partial C_A}{\partial z} + U A_c C_A \end{aligned}\right\} \longrightarrow U A_c C_A(0^-) = -A_c D_a \left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + U A_c C_A(0^+)$$

$$\xrightarrow{C_A(0^-) = C_{A0}} C_{A0} = -\frac{D_a}{U}\left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + C_A(0^+)$$

At z=L

$$C_A(L^-) = C_A(L^+)$$

$$\frac{\partial C_A}{\partial z} = 0$$

open-open vessel

$$-\frac{D_a}{U}\left(\frac{\partial C_A}{\partial z}\right)_{z=0^-} + C_A(0^-) = -\frac{D_a}{U}\left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + C_A(0^+)$$

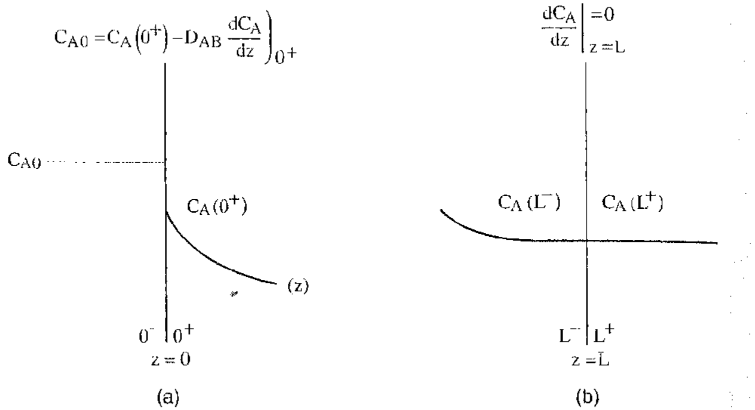


Figure 14-8 Schematic of Danckwerts boundary conditions. (a) Entrance (b) Exit

Back to the Solution for a Closed-Closed System

$$\frac{1}{Pe_r}\frac{d^2\psi}{d\lambda^2}-\frac{d\psi}{d\lambda}-Da\cdot\psi=0$$

$$\text{At } \lambda=0 \text{ then } 1=-\frac{1}{Pe_r}\left(\frac{d\psi}{d\lambda}\right)_{0^+}+\psi(0^+)$$

$$\text{At } \lambda=1 \text{ then } \frac{d\psi}{d\lambda}=0$$

$$\longrightarrow \psi_L=\frac{C_{AL}}{C_{A0}}=1-X=\frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_rq/2)-(1-q)^2(-Pe_rq/2)} \quad q=\sqrt{1+4Da/Pe_r}$$

$$\longrightarrow X=1-\frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_rq/2)-(1-q)^2(-Pe_rq/2)}$$

outside the limited case of a first-order reaction, a numerical solution of the equation is required, and because this is s split-boundary-value problem, an iterative technique is required.

Finding D_a and Peclet Number

1.Laminar flow with radial and axial molecular diffusion theory
2.Correlation from the literature for pipes and packed beds
3.Experimental tracer data

Dispersion in a Tubular Reactor with Laminar Flow

The axial velocity varies in the radial direction according to the Hagen-Poiseuille equation:

$$u(r) = 2U\left[1-\left(\frac{r}{R}\right)^2\right]$$

U is the average velocity

$$E(t) = \begin{cases} 0 \bullet\bullet\bullet\bullet t & < \tau/2 \\ \dfrac{\tau^2}{2t^3} \bullet\bullet t & \geq \tau/2 \end{cases} \bullet\bullet\bullet$$

In arriving at this distribution E(t), it was assumed that there are no transfer of molecules in the radial direction between streamlines.

$$r = 0 \bullet\bullet\bullet\bullet\bullet\bullet u \quad = 2U \bullet\bullet\bullet\bullet\bullet t \quad = \tau/2$$

$$r = 3R/4 \bullet\bullet\bullet u \quad = 7U/8 \bullet\bullet\bullet t \quad = 8\tau/7 \bullet$$

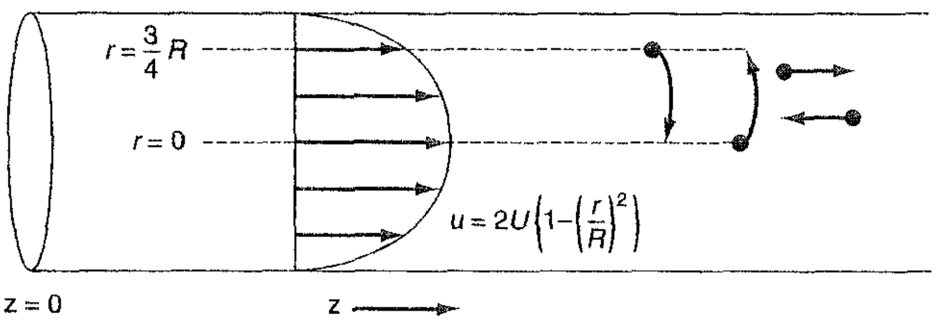


Figure 14-9 Radial diffusion in laminar flow.

In addition to the molecules diffusing between streamlines, they can also move forward or backward relative to the average fluid velocity by molecular diffusion (Fick's law).

The convective-diffusion equation for solute (e.g., tracer) transport in both the axial and radial direction can be obtained.

$$\frac{\partial C}{\partial t} + u(r)\frac{\partial C}{\partial z} = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{\partial^2 C}{\partial z^2}\right]$$

$$\xrightarrow{z^* = z - Ut} \left(\frac{\partial C}{\partial t}\right)_{z^*} + [u(r) - U]\frac{\partial C}{\partial z^*} = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{\partial^2 C}{\partial z^{*2}}\right]$$

$$\longrightarrow \overline{C}(z,t) = \frac{1}{\pi R^2}\int_0^R C(r,z,t)2\pi r dr$$

$$\frac{\partial \overline{C}}{\partial t} + U\frac{\partial \overline{C}}{\partial z^*} = D^*\frac{\partial^2 \overline{C}}{\partial z^{*2}}$$

D* is the Aris-Taylor dispersion coefficient

$$D^* = D_{AB} + \frac{U^2R^2}{48D_{AB}}$$

For laminar flow in a pipe

$$D_a \equiv D^*$$

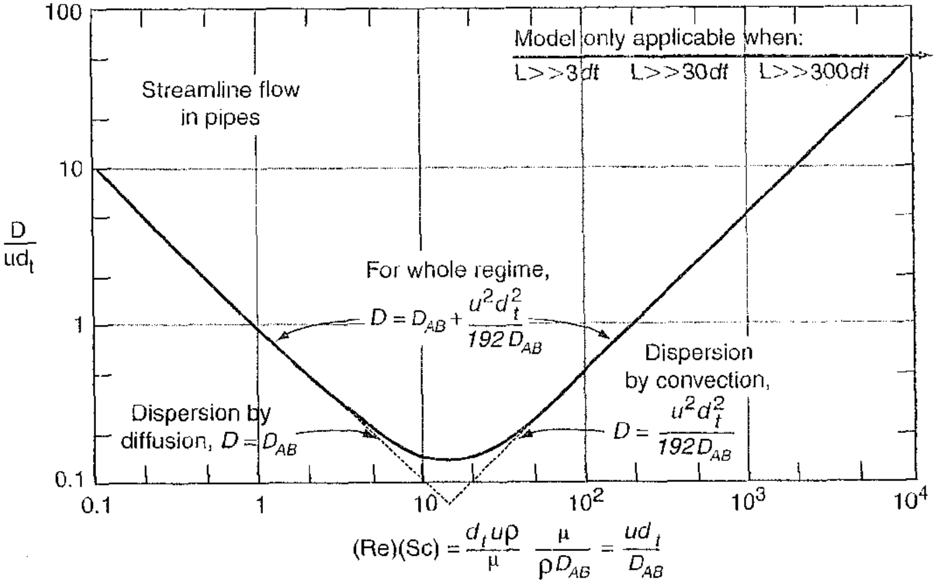


Figure 14-10 Correlation for dispersion for streamline flow in pipes. (From O. Levenspiel, Chemical Reaction Engineering, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [Note: $D \equiv D_a$ and $D \equiv D_{AB}$]

Correlations for D_a

Dispersion for Laminar and Turbulent Flow in Pipes

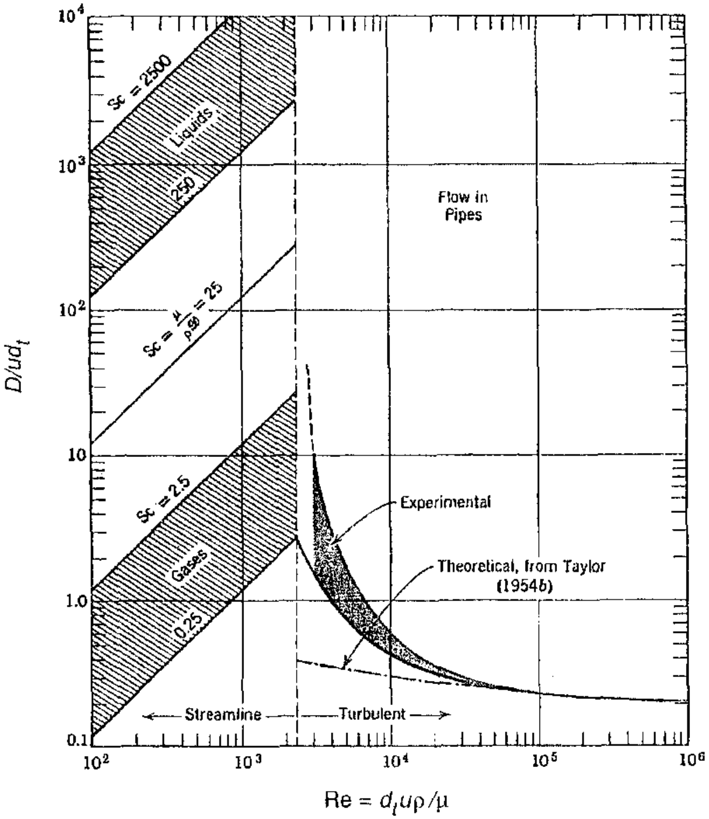


Figure 14-11 Correlation for dispersion of fluids flowing in pipes. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

d_t is the tube diameter

Sc is the Schmidt number

Dispersion in Packed Beds

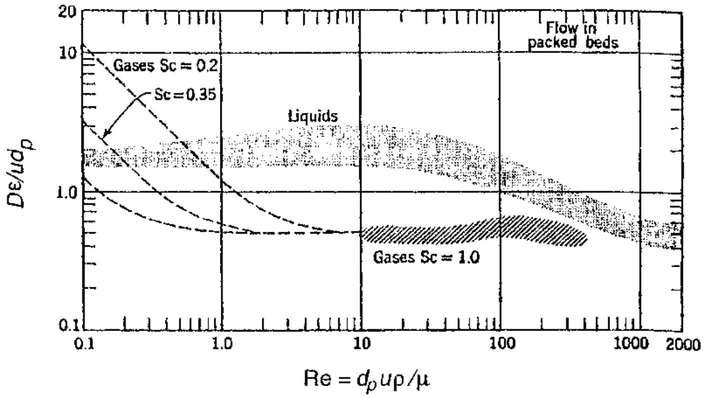


Figure 14-12 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

d_p is the particle diameter

ε is the porosity

Experimental Determination of D_a

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (U C_T)}{\partial z} = \frac{\partial C_T}{\partial t}$$

For the different types of boundary conditions at the reactor entrance and exit, to solve for the exit concentration as a function of dimensionless time ($\Theta = t/\tau$), and then relate D_a, σ^2, and τ.

Unsteady-State Tracer Balance

$$\xrightarrow{\psi = \frac{C_T}{C_{T0}},\quad \lambda = \frac{z}{L},\quad \Theta = \frac{tU}{L}} \quad \frac{1}{Pe_r}\frac{\partial^2 \psi}{\partial \lambda^2} - \frac{\partial \psi}{\partial \lambda} = \frac{\partial \Psi}{\partial \Theta}$$

Initial condition

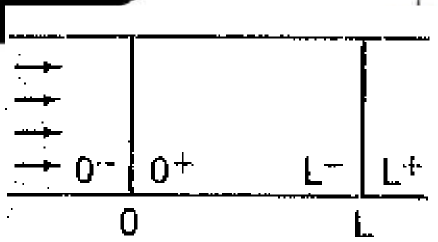
$$t > 0,\quad z > 0,\quad C_T(0^+, 0) = 0,\quad \psi(0^+) = 0$$

Mass of tracer injected, M is

$$M = U A_C \int_0^\infty C_T(0^-, t)\,dt$$

For a pulse input, C_{T0} is defined as the mass of tracer injected, M, divided by the vessel volume, V.

Solution for a Closed-Closed System



At λ=0

$$C_{T0} = -\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=0^+} + C_T(0^+) \longrightarrow \left(-\frac{1}{Pe_r}\frac{\partial \psi}{\partial \lambda}\right)_{0^+} + \psi(0^+) = 1$$

At λ=1

$$\frac{\partial C_A}{\partial z} = 0 \longrightarrow \frac{\partial \psi}{\partial \lambda} = 0$$

$$\longrightarrow t_m = \tau \longrightarrow \frac{\sigma^2}{t_m^2} = \frac{1}{\tau^2}\int_0^\infty (t-\tau)^2 E(t)dt$$

$$\longrightarrow \frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}\left(1 - e^{-Pe_r}\right)$$

RTD data $\longrightarrow \begin{matrix} t_m \\ \sigma^2 \end{matrix} \longrightarrow Pe_r \longrightarrow D_a$

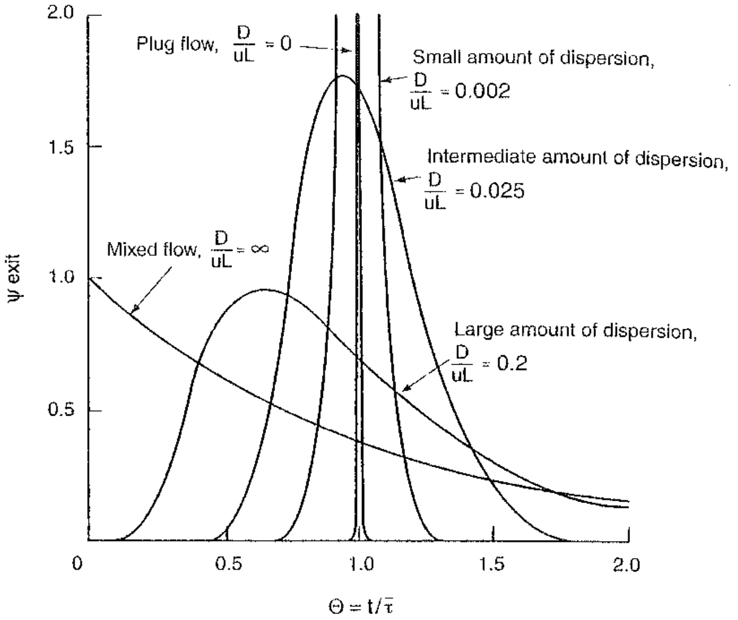


Figure 14-13 *C* curves in closed vessels for various extents of back-mixing as predicted by the dispersion model. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note:* $D \equiv D_a$][10]

Solution for a Open-Open System

At λ=0

$$-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=0^-}+C_T(0^-,t)=-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=0^+}+C_T(0^+,t) \qquad C_T(0^-,t)=C_T(0^+,t)$$

At λ=1

$$-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=L^-}+C_T(L^-,t)=-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=L^+}+C_T(L^+,t) \qquad C_T(L^-,t)=C_T(L^+,t)$$

Consider the case when there is no variation in the dispersion coefficient for all z and an impulse of tracer is injected at z=0 at t=0.

For long tubes (Pe>100) in which the concentration gradient at ±∞ will be zero

$$\longrightarrow \quad \psi(1,\Theta)=\frac{C_T(L,t)}{C_{T0}}=\frac{1}{2\sqrt{\pi\Theta/Pe_r}}\exp\left[\frac{-(1-\Theta)^2}{4\Theta/Pe_r}\right]$$

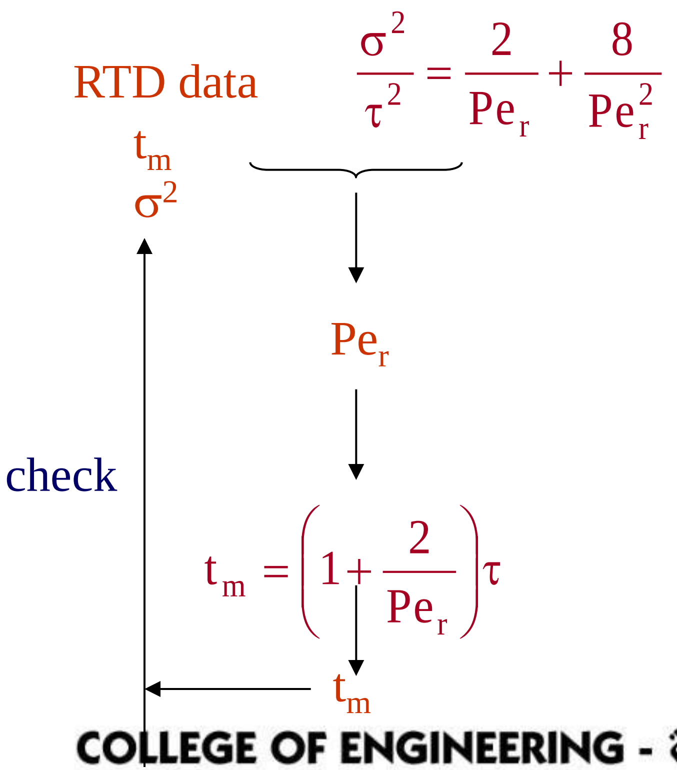
$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

τ is based on the volume between z=0 and z=L (i.e., reactor volume measured with a yardstick).

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

The mean residence time for an open system is greater than that for a closed-system. The reason is that the molecules can diffuse back into the reactor after they exit.

Case 1~space time τ is known



RTD data

t_m

σ^2

$$\underbrace{\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}}$$

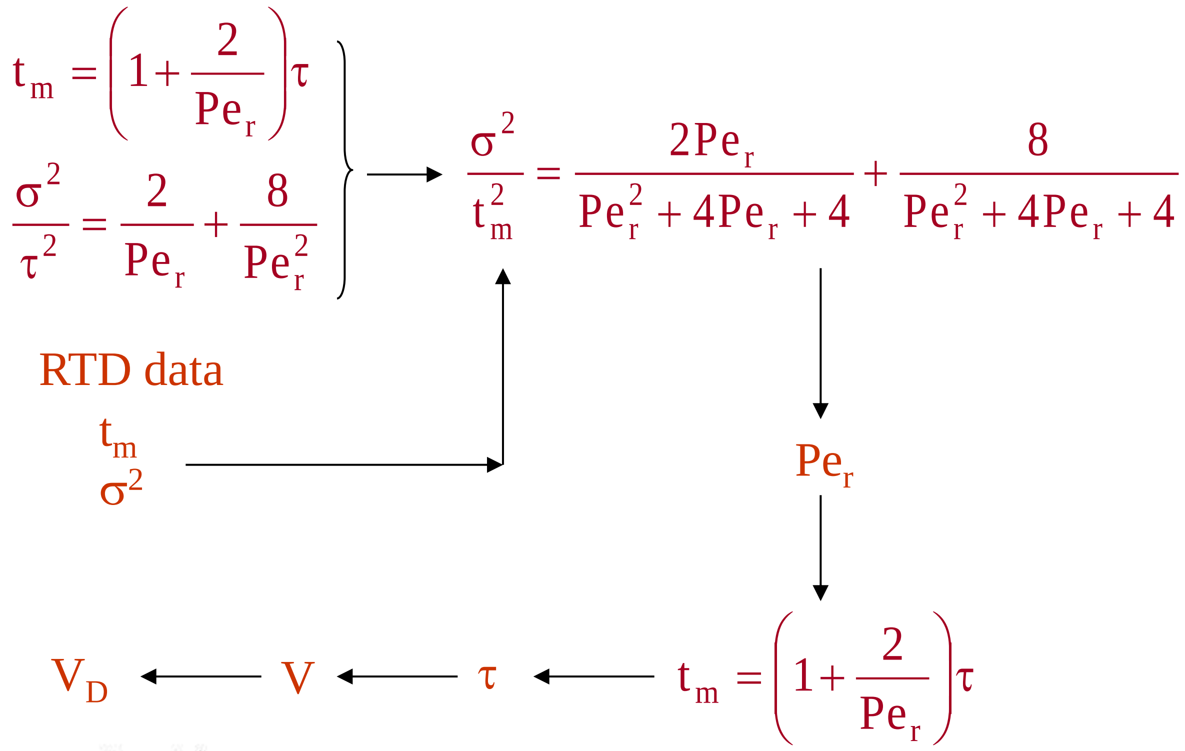
Pe_r

$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

t_m

check

Case 2~space time τ is unknown



$$\left.\begin{aligned} t_m &= \left(1 + \frac{2}{Pe_r}\right)\tau \\ \frac{\sigma^2}{\tau^2} &= \frac{2}{Pe_r} + \frac{8}{Pe_r^2} \end{aligned}\right\} \rightarrow \frac{\sigma^2}{t_m^2} = \frac{2Pe_r}{Pe_r^2 + 4Pe_r + 4} + \frac{8}{Pe_r^2 + 4Pe_r + 4}$$

RTD data

t_m

σ^2

Pe_r

$$V_D \longleftarrow V \longleftarrow \tau \longleftarrow t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

Sloppy Tracer Inputs

It is not always possible to inject a tracer pulse cleanly as an input to a system because it takes a finite time to inject the reactor.

When the injection does not approach a perfect input (Figure 14-14), the differences in the variances between the input and output tracer measurements are used to calculate the Peclet number:

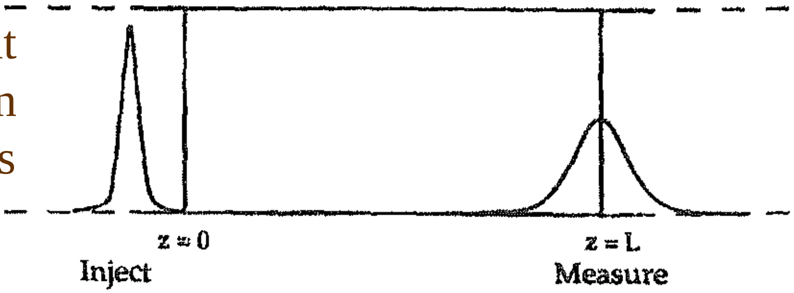


Figure 14-14 Imperfect tracer input.

$$\Delta\sigma^2 = \sigma_{in}^2 - \sigma_{out}^2$$

σ_{in}^2 is the variance of the tracer measured at some point upstream (near the entrance)

σ_{out}^2 is the variance of the tracer measured at some point downstream (after the exit)

For an open-open system

$$\frac{\Delta\sigma^2}{t_m^2} = \frac{2}{Pe_r}$$

Tanks-in-Series Model Versus Dispersion Model

For first-order reactions, the two models can be applied with equal ease.

However, the tanks-in-series model is mathematically easier to use to obtain the effluent concentration and conversion for reaction orders other than one and for multiple reactions.

These two models are equivalent when the Peclet-Bodenstein number is related to the number of tanks in series, n, by the equation

$$Bo = 2(n-1) \longrightarrow n = \frac{Bo}{2} + 1$$

$Bo = UL/D_a$
U is the superficial velocity
L is the reactor length
D_a is the dispersion coefficient

$$n = \frac{Bo}{2} + 1 = \frac{7.5}{2} + 1 = 4.75$$

$$n = \frac{\tau^2}{\sigma^2} = \frac{(5.15)^2}{6.1} = 4.35$$

$\longrightarrow$ For reactions other than first order,

$X(n=4) < X < X(n=5)$

Example 3-2

The first-order reaction

$$A \rightarrow B$$

is carried out in a 10-cm-diameter tubular reactor 6.36 m in length. The specific reaction rate is 0.25 min^{-1}. The results of a tracer test carried out this reactor are shown in Table E14-2.1.

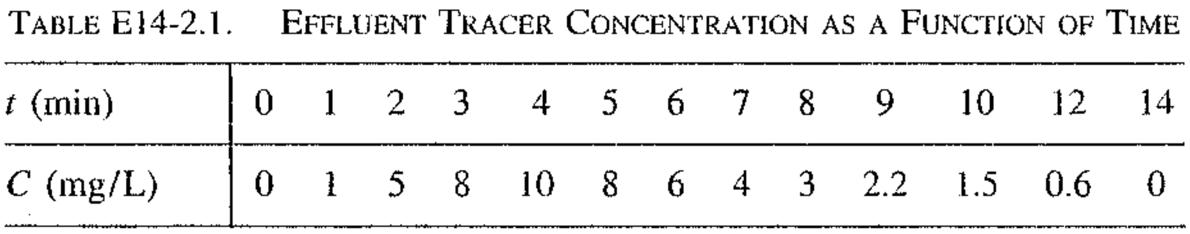


TABLE E14-2.1. EFFLUENT TRACER CONCENTRATION AS A FUNCTION OF TIME

t (min)	0	1	2	3	4	5	6	7	8	9	10	12	14
C (mg/L)	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0

Calculate conversion using (a) the closed vessel dispersion model, (b) PFR, (c) the tanks-in-series model, and (d) a single CSTR.

Solution

(a)

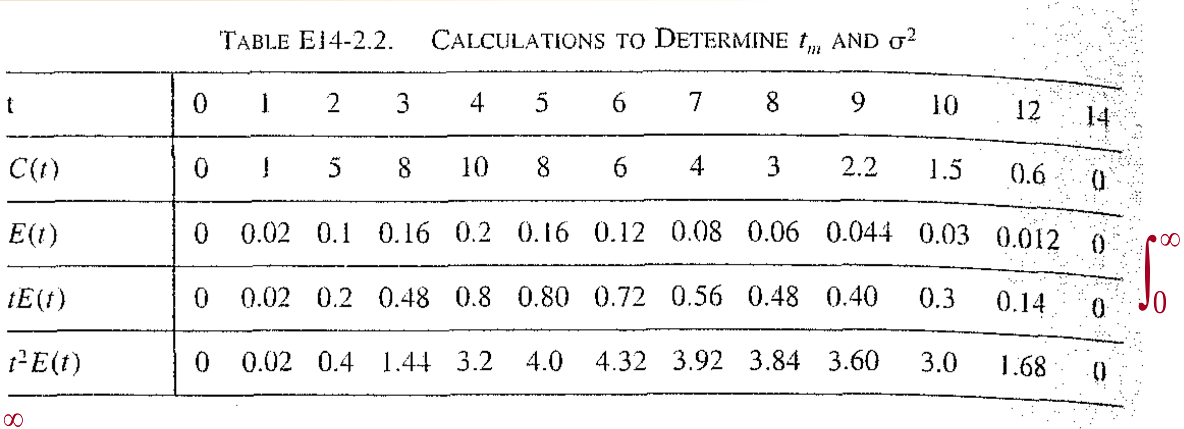


TABLE E14-2.2. CALCULATIONS TO DETERMINE t_m AND σ^2

t	0	1	2	3	4	5	6	7	8	9	10	12	14
$C(t)$	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
$E(t)$	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0
$tE(t)$	0	0.02	0.2	0.48	0.8	0.80	0.72	0.56	0.48	0.40	0.3	0.14	0
$t^2E(t)$	0	0.02	0.4	1.44	3.2	4.0	4.32	3.92	3.84	3.60	3.0	1.68	0

$$\int_0^\infty C(t)dt = 50\cdot g\cdot \min$$

$$t_m = \int_0^\infty tE(t)dt = 5.15\cdot \min$$

$$\sigma^2 = \int_0^\infty (t-t_m)^2E(t)dt = \int_0^\infty t^2E(t)dt - t_m^2 = 32.63-(5.15)^2 = 6.10\cdot \min^2$$

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}(1-e^{-Pe_r}) \longrightarrow \frac{6.1}{(5.15)^2} = 0.23 = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}(1-e^{-Pe_r}) \longrightarrow Pe_r = 7.5$$

$$Da = \tau k = t_m k = (5.15\cdot \min)(0.25\cdot \min^{-1}) = 1.29 \longrightarrow$$

$$q = \sqrt{1+\frac{4Da}{Pe_r}} = \sqrt{1+\frac{4(1.29)}{7.5}} = 1.30$$

$$\frac{Pe_r q}{2} = \frac{(7.5)(1.3)}{2} = 4.87$$

$$\longrightarrow X = 1 - \frac{4(1.30)\exp(7.5/2)}{(1+1.3)^2\exp(4.87)-(1-1.3)^2(-4.87)} = 0.68$$

(b)

$$X = 1 - e^{-\tau k} = 1 - e^{-Da} = 1 - e^{-1.29} = 0.725$$

(c)

$$n = \frac{\tau^2}{\sigma^2} = \frac{(5.15)^2}{6.1} = 4.35$$

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n}k\right)^n} = 1 - \frac{1}{(1 + 1.29/4.35)^{4.35}} = 0.677$$

(d)

$$X = \frac{\tau k}{1 + \tau k} = \frac{1.29}{1 + 1.29} = 0.563$$

$\longrightarrow$

PFR: X=72.5%

Dispersion: X=68.0%

Tanks in series: X=67.7%

Single CSTR: X=56.3%