



FLOW REACTORS FOR HOMOGENOUS REACTION: PERFORMANCE EQUATIONS AND APPLICATIONS



LEARNING OBJECTIVES

- At the end of this week's lecture, students should be able to:
 - Develop and apply the performance equation for plug flow reactors.
 - Compare the performance of the various reactors analytically or graphically



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PLUG FLOW REACTOR PERFORMANCE EQUATION

- In PFR the composition of the fluid varies from point to point along a flow path
- hence, the material balance for a differential element of volume dV becomes
- From the figure,
- input of $\mathbf{A} = \mathbf{F}_A$ moles/time
- output of $\mathbf{A} = \mathbf{F}_{A} + d\mathbf{F}_{A}$ moles/time

 disappearance of A by reaction = (-r_A)dV moles/time



3-1

input = output + disappearance by reaction + accumulation

• Substituting for each term in the material balance equation yields,

$$F_{\rm A} = (F_{\rm A} + dF_{\rm A}) + (-r_{\rm A})dV$$

PLUG FLOW REACTOR PERFORMANCE EQUATION

Note that

$$dF_{\rm A} = d[F_{\rm A0}(1 - X_{\rm A})] = -F_{\rm A0}dX_{\rm A}$$

Substituting for dF_A in eqn.3-1 and rearranging yields

$$F_{\rm A0}dX_{\rm A} = (-r_{\rm A})dV \qquad 3-2$$

- Eqn.3-2 accounts for A in the differential section of reactor of volume dV. For the reactor as a whole the expression must be integrated.
- NB F_{A0} is constant, but r_A is dependent on the concentration or conversion of materials. Grouping the terms accordingly yields,

$$\int_{0}^{V} \frac{dV}{F_{A0}} = \int_{0}^{X_{Af}} \frac{dX_{A}}{-r_{A}}$$
• Thus, for any \mathcal{E}_{A}

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_{0}^{X_{Af}} \frac{dX_{A}}{-r_{A}}$$
• or
$$\tau = \frac{V}{v_{0}} = \frac{VC_{A0}}{F_{A0}} = C_{A0} \int_{0}^{X_{Af}} \frac{dX_{A}}{-r_{A}}$$
3-3

PLUG FLOW REACTOR PERFORMANCE EQUATION

- Eqn.3-3 allows the determination of reactor size for a given feed rate and required conversion in a PFR.
- The difference between PFR and MFR is that r_A varies in PFR, but remains constant in MFR.
- A more general expression for PFR, if the feed on which conversion is based, subscript 0, enters the reactor partially converted, subscript i, and leaves at a conversion designated by subscript f, we have $V = \int_{X_{Af}} dX_A$

$$\frac{V}{F_{A0}} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$
$$= C_{A0} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$
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For a case of constant-density systems,

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$$X_{\rm A} = 1 - \frac{C_{\rm A}}{C_{\rm A0}}$$
 and $dX_{\rm A} = -\frac{dC_{\rm A}}{C_{\rm A0}}$

 the performance equation Eqn.3-3 can be expressed in terms of concentrations, or conversion as

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PLUG FLOW REACTOR PERFORMANCE EQUATION

• For
$$\mathcal{E}_{A} = 0$$
, $\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_{0}^{X_{Af}} \frac{dX_{A}}{-r_{A}} = -\frac{1}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_{A}}{-r_{A}}$
• or $\tau = \frac{V}{v_{0}} = C_{A0} \int_{0}^{X_{Af}} \frac{dX_{A}}{-r_{A}} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_{A}}{-r_{A}}$

• or as graphically represented below.



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SPECIAL CASES

- For systems of changing density it is more convenient to use conversions.
- Whatever its form, the performance equations interrelate the rate of reaction, the extent of reaction, the reactor volume, and the feed rate, and if any one of these quantities is unknown it can be found from the other three.
- For Zero-order homogeneous reaction, any constant $\mathcal{E}_{\mathcal{A}}$,

$$k\tau = \frac{kC_{\rm A0}V}{F_{\rm A0}} = C_{\rm A0}X_{\rm A}$$

For first-order irreversible reaction,

$$A \longrightarrow Product, \qquad \text{any constant } \mathcal{E}_{\mathcal{A}},$$
$$k\tau = -(1 + \varepsilon_{A}) \ln (1 - X_{A}) - \varepsilon_{A} X_{A}$$

• For first-order reversible reaction, $\mathbf{A} \longleftrightarrow \mathbf{r}\mathbf{R}$, $C_{R0}/C_{A0} = M$, kinetics approximated or fitted by $-\mathbf{r}_{\mathbf{A}} = \mathbf{k}_{l}\mathbf{C}_{\mathbf{A}} - \mathbf{k}_{2}\mathbf{C}_{\mathbf{R}}$ with an observed equilibrium conversion \mathbf{X}_{Ae} , any constant \mathcal{E}_{A} ,

$$k_{1}\tau = \frac{M + rX_{Ae}}{M + r} \left[-(1 + \varepsilon_{A}X_{Ae})\ln\left(1 - \frac{X_{A}}{X_{Ae}}\right) - \varepsilon_{A}X_{A} \right]$$



SPECIAL CASES

• Second-order irreversible reaction, $\mathbf{A} + \mathbf{B} \longrightarrow \text{products with}$ equimolar feed or $\mathbf{2A} \longrightarrow \text{products, any constant } \mathcal{E}_{\mathcal{A}}$,

$$C_{A0}k\tau = 2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A+1)^2 \frac{X_A}{1-X_A}$$

• EXAMPLE 1

A homogeneous gas reaction A \longrightarrow 3R has a reported rate at 215°C

 $-r_{\rm A} = 10^{-2} C_{\rm A}^{1/2}$. [mol/liter sec]

Find the space-time needed for 80% conversion of a 50% A-50% inert feed to a plug flow reactor operating at 215°C and 5 atm ($C_{A0} = 0.0625$ mol/liter).





SOLUTION

- From the stoichiometry,
- And PFR performance eqn, becomes

$$\varepsilon_{\rm A} = \frac{4-2}{2} = 1$$
$$\tau = C_{\rm A0} \int_0^{X_{\rm Af}} \frac{dX_{\rm A}}{-r_{\rm A}}$$

$$= C_{A0} \int_{0}^{X_{Af}} \frac{dX_{A}}{kC_{A0}^{1/2} \left(\frac{1 - X_{A}}{1 + \varepsilon_{A}X_{A}}\right)^{1/2}}$$

$$=\frac{C_{\rm A0}^{1/2}}{k}\int_0^{0.8} \left(\frac{1+X_{\rm A}}{1-X_{\rm A}}\right)^{1/2} dX_{\rm A}$$

 The integral can be evaluated either graphically or numerically.

• Graphical Integration.

 First evaluate the function to be integrated at selected values (see Table) and plot this function (see Figure)

X _A	$\frac{1+X_{\rm A}}{1-X_{\rm A}}$	$\left(\frac{1+X_{\rm A}}{1-X_{\rm A}}\right)^{1/2}$
0	1	1
0.2	$\frac{1.2}{0.8} = 1.5$	1.227
0.4	2.3	1.528
0.6	4	2
0.8	9	. 3



SOLUTION





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Numerical Integration. Using Simpson's rule,

(Recall from CHE 326) applicable to an even number of uniformly spaced intervals on the $\mathbf{X}_{\mathbf{A}}$ axis, we find for the data in the Table

Area =
$$\int_{0}^{0.8} \left(\frac{1+X_{\rm A}}{1-X_{\rm A}}\right)^{1/2} dX_{\rm A}$$

= (average height)(total width)

$$= \left[\frac{1(1) + 4(1.227) + 2(1.528) + 4(2) + 1(3)}{12}\right] (0.8)$$

EXAMPLE 2

The homogeneous gas decomposition of phosphine $4PH_3(g) \rightarrow P_4(g) + 6H_2$

proceeds at 649°C with the first-order rate

 $-r_{\rm PH_3} = (10/{\rm hr}) \, {\rm C}_{\rm PH_3}$

What size of plug flow reactor operating at 649°C and 460 kPa can produce 80% conversion of a feed consisting of 40 mole of pure phosphine per hour?





New York

EXAMPLE 2 SOLUTION

• The volume of plug flow reactor is given by

$$V = \frac{F_{A0}}{kC_{A0}} \left[\left(1 + \varepsilon_A \right) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A \right]$$

Evaluating the individual terms in this expression gives

$$F_{\rm A0} = 40 \text{ mol/hr}$$
 $k = 10/\text{hr}$ $X_{\rm A} = 0.8$

• And
$$C_{A0} = \frac{p_{A0}}{\mathbf{R}T} = \frac{460\,000\,\mathrm{Pa}}{(8.314\,\mathrm{Pa}\cdot\mathrm{m^3/mol}\cdot\mathrm{K})(922\,\mathrm{K})} = 60\,\mathrm{mol/m^3}$$

- Calculating $\varepsilon_{\rm A} = \frac{7-4}{4} = 0.75$
- Substituting for all the terms in the expression above,

$$\frac{V}{=} = \frac{40 \text{ mol/hr}}{(10/\text{hr})(60 \text{ mol/m}^3)} \left[(1 + 0.75) \ln \frac{1}{0.2} - 0.75(0.8) \right]$$
$$= 0.148 \text{ m}^3 = \underline{148 \text{ liters}}$$

EXAMPLE 3

We suspect that the gas reaction between A, B, and R is an elementary reversible reaction

$$A + B \xrightarrow{k_1 \atop k_2} R$$

and we plan to test this with experiments in an isothermal plug flow reactor.

(a) Develop the isothermal performance equation for these kinetics for a feed of A, B, R, and inerts.

(b) Show how to test this equation for an equimolar feed of A and B.

Solution:

(a) For this elementary reaction the rate wrt component A is

$$-r_{\rm A} = k_1 C_{\rm A} C_{\rm B} - k_2 C_{\rm R} = k_1 \frac{N_{\rm A}}{V} \frac{N_{\rm B}}{V} - k_2 \frac{N_{\rm R}}{V}$$

And at constant pressure we have,

$$-r_{\rm A} = k_1 \frac{N_{\rm A0} - N_{\rm A0} X_{\rm A}}{V_0 (1 + \varepsilon_{\rm A} X_{\rm A})} \frac{N_{\rm B0} - N_{\rm A0} X_{\rm A}}{V_0 (1 + \varepsilon_{\rm A} X_{\rm A})} - k_2 \frac{N_{\rm R0} + N_{\rm A0} X_{\rm A}}{V_0 (1 + \varepsilon_{\rm A} X_{\rm A})}$$







EXAMPLE 3 SOLUTION

• Letting M =
$$C_{B0}/C_{A0}$$
 and M' = C_{R0}/C_{A0} , we obtain
 $-r_A = k_1 C_{A0}^2 \frac{(1 - X_A)(M - X_A)}{(1 + \varepsilon_A X_A)^2} - k_2 C_{A0} \frac{M' + X_A}{1 + \varepsilon_A X_A}$

Hence, the design equation for PFR is given as

$$\tau = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

• Substituting for $-r_A$ yields,

$$\tau = \int_0^{X_{Af}} \frac{(1 + \varepsilon_A X_A)^2 dX_A}{k_1 C_{A0} (1 - X_A) (M - X_A) - k_2 (M' + X_A) (1 + \varepsilon_A X_A)}$$

- Thus \boldsymbol{E}_A accounts for the stoichiometry and for inerts present in the feed.
- (b) For equimolar feed of A and B,

$$C_{A0} = C_{B0}$$
, and $C_{R0} = 0$, and no inerts.

• Also we have M = 1, M' = 0, and $\mathcal{E}_A = -0.5$; hence the earlier expression for part a reduces to



EXAMPLE 3 SOLUTION

$$\tau = \int_{0}^{X_{Af}} \frac{(1 - 0.5X_{A})^{2} dX_{A}}{k_{1}C_{A0}(1 - X_{A})^{2} - k_{2}X_{A}(1 - 0.5X_{A})}$$
$$\int_{0}^{X_{Af}} f(X_{A}) dX_{A}.$$

- Let's call this
- With V, v_0 and X_A data from a series of experiments, the left side and the right side of Eq. (i) are separately evaluated.
 - For the right side, at various X_A evaluate $f(X_A)$, then integrate graphically to give $\int f(X_A) dX_A$ and then make the plot of Figure shown.
 - If the data fall on a straight line, then the suggested kinetic scheme can be said to be satisfactory in that it fits the data.



SUMMARY OF PERFORMANCE EQUATION FOR IDEAL REACTORS

Performance Equations for *n*th-order Kinetics and $\varepsilon_A \neq 0$

	Plug Flow	
n = 0 $-r_{\rm A} = k$	$\frac{k\tau}{C_{A0}} = X_A$	
n = 1 $-r_{\rm A} = kC_{\rm A}$	$k\tau = (1 + \varepsilon_{\rm A}) \ln \frac{1}{1 - X_{\rm A}} - \varepsilon_{\rm A} X_{\rm A}$	
n = 2 $-r_{\rm A} = kC_{\rm A}^2$	$k\tau C_{A0} = 2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A+1)^2 \cdot \frac{X_A}{1-X_A}$	
$any n -r_A = kC_A^n$		
n = 1		
$A \stackrel{1}{\stackrel{2}{\underset{2}{\longrightarrow}}} rR$	$\frac{k\tau}{X_{Ae}} = (1 + \varepsilon_A X_{Ae}) \ln \frac{X_{Ae}}{X_{Ae} - X_A} - \varepsilon_A X_A$	
$C_{R0} = 0$		
General expression	$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A}$	

SUMMARY OF PERFORMANCE EQUATION FOR IDEAL REACTORS

Performance Equations for <i>n</i> th-order Kinetics and $\varepsilon_A = 0$			
	Plug Flow or Batch		
$n = 0$ $-r_{\rm A} = k$	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$		
$n = 1$ $-r_{\rm A} = kC_{\rm A}$	$k\tau = \ln \frac{C_{A0}}{C_A} = \ln \frac{1}{1 - X_A}$		
$n = 2$ $-r_{\rm A} = kC_{\rm A}^2$	$k\tau C_{A0} = \frac{C_{A0} - C_{A}}{C_{A}} = \frac{X_{A}}{1 - X_{A}}$		
$any n -r_A = kC_A^n$	$(n-1)C_{A0}^{n-1}k\tau = \left(\frac{C_A}{C_{A0}}\right)^{1-n} - 1 = (1-X_A)^{1-n} - 1$		
$n = 1$ $A \stackrel{1}{\underset{2}{\overset{2}{\xleftarrow}}} R$	$k_1 \tau = \left(1 - \frac{C_{Ae}}{C_{A0}}\right) \ln\left(\frac{C_{A0} - C_{Ae}}{C_A - C_{Ae}}\right) = X_{Ae} \ln\left(\frac{X_{Ae}}{X_{Ae} - X_A}\right)$		
$C_{\rm R0}=0$			
General rate	$\tau = \int_{C_{\rm A}}^{C_{\rm A0}} \frac{dC_{\rm A}}{-r_{\rm A}} = C_{\rm A0} \int_{0}^{X_{\rm Ac}} \frac{dX_{\rm A}}{-r_{\rm A}}$		

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SUMMARY OF PERFORMANCE EQUATION FOR IDEAL REACTORS

Performance Equations for nth-order Kinetics

	-	
	Mixed Flow $\varepsilon_A = 0$	Mixed Flow $\varepsilon_{\rm A} \neq 0$
$n = 0$ $-r_{\rm A} = k$	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$	$\frac{k\tau}{C_{\rm A0}} = X_{\rm A}$
$n = 1$ $-r_{\rm A} = kC_{\rm A}$	$k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A}$	$k\tau = \frac{X_{\rm A}(1+\varepsilon_{\rm A}X_{\rm A})}{1-X_{\rm A}}$
$n = 2$ $-r_{\rm A} = kC_{\rm A}^2$	$k\tau = \frac{(C_{A0} - C_A)}{C_A^2} = \frac{X_A}{C_{A0}(1 - X_A)^2}$	$k\tau C_{A0} = \frac{X_A (1 + \varepsilon_A X_A)^2}{(1 - X_A)^2}$
any n $-r_{\rm A} = kC_{\rm A}^n$	$k\tau = \frac{C_{A0} - C_A}{C_A^n} = \frac{X_A}{C_{A0}^{n-1}(1 - X_A)^n}$	$k\tau C_{A0}^{n-1} = \frac{X_{A}(1+\varepsilon_{A}X_{A})^{n}}{(1-X_{A})^{n}}$
$n = 1$ $A \stackrel{1}{\underset{2}{\longleftarrow}} R$	$k_{1}\tau = \frac{(C_{A0} - C_{A})(C_{A0} - C_{Ae})}{C_{A0}(C_{A} - C_{Ae})} = \frac{X_{A}X_{Ae}}{X_{Ae} - X_{A}}$	$\frac{k\tau}{X_{Ae}} = \frac{X_A(1 + \varepsilon_A X_A)}{X_{Ae} - X_A}$
$\frac{C_{\rm R0} = 0}{\rm General \ rate}$	$\tau = \frac{C_{A0} - C_A}{-r} = \frac{C_{A0}X_A}{-r}$	$\tau = \frac{C_{A0}X_{A}}{-r}$
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THANK YOU FOR YOUR **ATTENTION! ANY QUESTIONS?**