CL223 CHEMICAL REACTION ENGINEERING-I

MODULE

II

INTERPRETATION OF BATCH REACTOR DATA

Lecture Notes:
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Reactor Design and Analysis of Performance

- Reactor design embodies many different facets and disciplines, the details of some of which are outside our scope. here, we focus on process design as opposed to mechanical design of equipment . Other aspects are implicit, but are not treated explicitly: instrumentation and process control, economic, and socioeconomic (environmental and safe-operation). Reactor design is a term we may apply to a new installation or modification;

- **Parameters Affecting Reactor Performance:** The term “reactor performance” usually refers to the operating results achieved by a reactor, particularly with respect to fraction of reactant converted or product distribution for a given size and configuration; alternatively, it may refer to size and configuration for a given conversion or distribution. In any case, it depends on two main types of behavior: (1) rates of processes involved, including reaction and heat and mass transfer, sometimes influenced by equilibrium limitations; and (2) motion and relative-motion of elements of fluid (both single-phase and multiphase situations) and solid particles (where involved), whether in a flow system or not.

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- At this stage, type (1) is more apparent than type (2) and we provide some preliminary discussion of (2) here. Flow characteristics include relative times taken by elements of fluid to pass through the reactor (residence-time distribution), and mixing characteristics for elements of fluid of different ages: point(s) in the reactor at which mixing takes place, and the level of segregation at which it takes place (as a molecular dispersion or on a macroscopic scale). Lack of sufficient information on one or both of these types is a major impediment to a completely rational reactor design.

Interpretation of batch reactor data

- A rate equation characterizes the rate of reaction, and its form may either be suggested by theoretical considerations or simply be the result of an empirical curve-fitting procedure. In any case, the value of the constants of the equation can only be found by experiment; predictive methods are inadequate at present.
- The determination of the rate equation is usually a two-step procedure; first the concentration dependency is found at fixed temperature and then the temperature dependence of the rate constants is found, yielding the complete rate equation.
- Equipment by which empirical information is obtained can be divided into two types, the batch and *flow reactors*. *The batch reactor is simply a container* to hold the contents while they react. All that has to be determined is the extent of reaction at various times, and this can be followed in a number of ways, for example:

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1. By following the concentration of a given component.
2. By following the change in some physical property of the fluid, such as the electrical conductivity or refractive index.
3. By following the change in total pressure of a constant-volume system.
4. By following the change in volume of a constant-pressure system.

- The experimental **batch reactor** is usually operated **isothermally** and at **constant volume** because it is easy to interpret the results of such runs.
- The **flow reactor** is used primarily in the study of the kinetics of **heterogeneous** reactions.
- There are two procedures for analyzing kinetic data, the ***integral*** *and the* ***differential*** *methods.*

Comparison of differential and integral method

Differential method	Integral method
In the differential method of analysis we test the fit of the rate expression to the data directly and without any integration. However, since the rate expression is a differential equation, we must first find (l/V)(dN/dt) from the data before attempting the fitting procedure.	In the integral method of analysis we guess a particular form of rate equation and, after appropriate integration and mathematical manipulation, predict that the plot of a certain concentration function versus time should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained, then the rate equation is said to satisfactorily fit the data.
The differential method is useful in more complicated situations but requires more accurate or larger amounts of data	The integral method is easy to use and is recommended when testing specific mechanisms, or relatively simple rate expressions.
the differential method can be used to develop or build up a rate equation to fit the data.	The differential method is useful in more complicated situations but requires more accurate or larger amounts of data

Constant-volume Batch Reactor

- When the constant-volume batch reactor is considered it refers to the volume of reaction mixture, and not the volume of reactor. Thus, this term actually means a *constant-density reaction system*.
- *Most liquid-phase reactions* as well as all gas-phase reactions occurring in a constant-volume bomb fall in this class.
- In a constant-volume system the measure of reaction rate of component i becomes

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{d(N_i/V)}{dt} = \frac{dC_i}{dt}$$

- For ideal gases

$$C_i = p_i / RT$$

$$r_i = \frac{d(p_i/RT)}{dt} = \frac{1}{RT}\frac{dp_i}{dt}$$

Analysis of Total Pressure Data Obtained in a Constant-Volume System

- For isothermal gas reactions where the number of moles of material changes during reaction, let us develop the general expression which relates the changing total pressure of the system π *to the changing concentration or partial pressure of* any of the reaction components.
- Let rate equation is

$$aA + bB + \ldots\ldots \rightarrow rR + sS + \ldots\ldots\ldots\ldots$$

- At time t =0 the amount of reactant and product along with inert are N_{A0}, N_{B0}…….. N_{R0}, N_{S0}. N_{inert}
- At time t the above amount are (N_{A0} –ax), (N_{B0} –bx),……. (N_{R0} +rx), (N_{S0} +sx), N_{inert}
- Let $N_0 = N_{A0} + N_{B0} + \ldots N_{R0} + N_{S0} \ldots\ldots\ldots\ldots + N_{inert}$
- At time t $N = N_0 + x(r+s+\ldots-a-b-\ldots) = N_0 + x.\Delta n$
- or

$$C_A = \frac{p_A}{RT} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V} = \frac{N_{A0}}{V} - \frac{a}{\Delta n}\frac{N - N_0}{V}$$

Conversion

- Suppose that N_{Ao} *is the initial amount of A in the reactor at time t = 0, and* that N_A *is the amount present at time t. Then the conversion of A in the constant* volume system is given by

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A / V}{N_{A0} / V} = 1 - \frac{C_A}{C_{A0}}$$

- or $$dX_A = -\frac{dC_A}{C_{A0}}$$

Integral Method of Analysis of Data

Type of reaction	reaction	Relation between conversion and time
Irreversible uni-molecular-type first order reaction	$A \rightarrow product$	$-\ln(1-X_A) = kt$
Irreversible Bimolecular-Type Second-Order Reactions	$A + B \rightarrow product$	$\int_0^{X_A} \frac{dX_A}{(1-X_A)(\frac{C_{B0}}{C_{A0}}-X_A)} = C_{A0}kt$
Irreversible Tri-molecular-Type Third-Order Reactions	$A + B + C \rightarrow product$	$\int_0^{X_A} \frac{dX_A}{(1-X_A)\left(\frac{C_{B0}}{C_{A0}}-X_A\right)\left(\frac{C_{C0}}{C_{A0}}-X_A\right)} = C_{A0}^2 kt$

Overall Order of Irreversible Reactions from the Half-Life

- The half-life of the reaction is defined *as the time needed for the concentration* of reactants to drop to one-half the original value.
- Let us consider the decay of reactant A as per following rate equation

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

- For n≠1

$$C_A{}^{1-n} - C_{A0}{}^{1-n} = k(n-1)t$$

- Therefore half-life is given by

$$t_{1/2} = \frac{(0.5)^{1-n} - 1}{k(n-1)} C_{A0}{}^{1-n}$$

- **Fractional Life Method**

$$t_F = \frac{(F)^{1-n} - 1}{k(n-1)} C_{A0}{}^{1-n}$$

- Thus, a plot of log t_F versus log C_{Ao}, *will give the reaction* order.

Mechanism of Irreversible Reactions in Parallel

- Consider the simplest case, A decomposing by two competing paths, both elementary reactions:

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

- The rates of change of the three components are given by

$$-r_A = -\frac{dC_A}{dt} = (k_1 + k_2)C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A$$

- The k values are found using all three differential rate equations.
- $-\ln\frac{C_A}{C_{A0}} = (k_1 + k_2)t$ and $\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} = \frac{C_R - C_{R0}}{C_S - C_{S0}}$
- Thus, the slope of a plot of C_R versus C_s gives the ratio k_1/k_2. *Knowing* k_1/k_2 *as well as* $k_1 + k_2$ *gives* k_1 *and* k_2.

Homogeneous Catalyzed Reactions

- Suppose the reaction rate for a homogeneous catalyzed system is the sum of rates of both the un-catalyzed and catalyzed reactions,

$$A \xrightarrow{k_1} R$$

$$A + C \xrightarrow{k_2} R + C$$

- And the corresponding rate equations are

$$-\left(\frac{dC_A}{dt}\right)_1 = k_1 C_A$$

$$-\left(\frac{dC_A}{dt}\right)_2 = k_2 C_A C_C$$

$$-\left(\frac{dC_A}{dt}\right)_{overall} = k_1 C_A + k_2 C_A C_C = (k_1 + k_2 C_C) C_A$$

- As concentration of catalyst remains unchanged

$$-\ln \frac{C_A}{C_{A0}} = (k_1 + k_2 C_C) t$$

Autocatalytic Reactions

- A reaction in which one of the products of reaction acts as a catalyst is called an autocatalytic reaction. The simplest such reaction with rate equation is

$$A + R \rightarrow R + R$$

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

- Because the total number of moles of A and R remain unchanged as A is consumed, we may write that at any time

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = cons\tan t$$

- So rate equation becomes $-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$

- By integrating the above equation we get

$$\ln\frac{C_R / C_{R0}}{C_A / C_{A0}} = (C_{A0} + C_{R0})kt$$

Continued…

- For an autocatalytic reaction in a batch reactor some product R must be present if the reaction is to proceed at all.
- Starting with a very small concentration of R, and the rate will rise as R is formed.
- At the other extreme, when A is just about used up the rate must drop to zero. This result is that the rate follows a parabola, with a maximum where the concentrations of A and R are equal.

Irreversible Reactions in Series

- Let us consider consecutive unimolecular first order reactions are in series and is given by:

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

- And the rate equations are

$$r_A = \left(\frac{dC_A}{dt}\right) = -k_1 C_A$$

$$r_R = \left(\frac{dC_R}{dt}\right) = k_1 C_A - k_2 C_R$$

$$r_S = \left(\frac{dC_S}{dt}\right) = k_2 C_R$$

- By integrating the first rate equation with respect to reactant A starting with initial concentration C_{A0} we get

$$-\ln\frac{C_A}{C_{A0}} = k_1 t \quad \text{or} \quad C_A = C_{A0} e^{-k_1 t}$$

Continued…

- To find the changing concentration of R, substitute the above expression form concentration of A from into the differential equation governing the rate of change of R, and the equation becomes

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t}$$

- The above differential equation will be solved with the help of integrating factor and the solution becomes

$$C_R = C_{A0} k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right)$$

- As there is no change in total number of moles, the stoichiometric relates the concentrations of reacting components by $C_{A0} = C_A + C_R + C_S$

- And $C_S = C_{A0} \left(1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$

Continued….

- **Special cases**
- **Case I:** Now if k_2 is much larger than k_1,

$$C_S = C_{A0}\left(1 - e^{-k_1 t}\right), \qquad k_2 \gg k_1$$

- In other words, the rate is determined by k_1 or the first step of the two-step reaction.
- **Case II:** If k_1 is much larger than k_2, then

$$C_S = C_{A0}\left(1 - e^{-k_2 t}\right), \qquad k_1 \gg k_2$$

- which is a first-order reaction governed by k_2, the slower step in the two-step reaction. Thus, in general, **for any number of reactions in series it is the slowest step that has the greatest influence on the overall reaction rate.**
- **Case III:** The time at which the maximum concentration of R occurs i.e.

$$dC_R/dt = 0.$$

- And the maximum time is

$$t_{\max} = \frac{1}{k_{\text{log mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

Continued…

- The maximum concentration of R is

$$\frac{C_{R,\max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}$$

- From the results for this particular reaction we can conclude that

1. A decreases exponentially, R rises to a maximum and then falls, and S rises continuously, the greatest rate of increase of S occurring where R is a maximum.
2. In particular, one can evaluate k_1 and k_2 by noting the maximum concentration of intermediate and the time when this maximum is reached.

First-Order Reversible Reactions

- Let us consider reactions for which complete conversion cannot be assumed. The simplest case is the opposed unimolecular-type reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R, \qquad K_C = K = \text{equilibrium constant}$$

- Starting with a concentration ratio $\boldsymbol{M = C_{A0}/C_{R0}}$ the rate equation is

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = k_1C_A - k_2C_R$$

$$= k_1(C_{A0} - C_{A0}X_A) - k_2(MC_{A0} + C_{A0}X_A)$$

- At equilibrium $\qquad dC_A/dt = 0$

- Therefore $\qquad K_C = \dfrac{C_{Re}}{C_{Ae}} = \dfrac{M + X_{Ae}}{1 - X_{Ae}}$

- And the equilibrium constant to be $\qquad K_C = \dfrac{k_1}{k_2}$

Continued…

- By combining the above equation the instantaneous conversion may be written in terms of equilibrium conversion as follows:

$$\frac{dX_A}{dt} = \frac{k_1 (M+1)}{M + X_{Ae}} (X_{Ae} - X_A)$$

- With conversions measured in terms of X_{Ae}, this may be looked on as a pseudo first-order irreversible reaction which on integration gives

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M+1}{M + X_{Ae}} k_1 t$$

- First- order irreversible reaction $-\ln(1 - X_A) = kt$

- NOTE: The similarity between equations for the first-order irreversible and reversible. The irreversible reaction is simply the special case of the reversible reaction in which C_A, = 0, or X_{Ae} = 1, or $Kc = \infty$

Second-Order Reversible Reactions

- For the bimolecular-type second order reactions
-
$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$$

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$$

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R$$

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R$$

- with the restrictions that $C_{A0} = C_{B0}$, and $C_{R0} = C_{S0} = 0$, the integrated rate equations for A and B are all identical, as follows

$$\ln \frac{X_{A_e} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A} = 2k_1 \left(\frac{1}{X_{Ae}} - 1 \right) C_{A0} t$$

Reactions of Shifting Order

- In searching for a kinetic equation it may be found that the data are well fitted by one reaction order at high concentrations but by another order at low concentrations. Let us consider such a reaction as follows:

$$A \rightarrow R \quad \text{with} \quad -r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A}$$

At high C_A (or $k_2 C_A \gg 1$)—the reaction is of zero order with rate constant k_1/k_2

At low C_A (or $k_2 C_A \ll 1$)—the reaction is of first order with rate constant k_1

- Now integrating the above equation we get

$$\ln \frac{C_{A0}}{C_A} + k_2 (C_{A0} - C_A) = k_1 t$$

- Or

$$\frac{C_{A0} - C_A}{\ln (C_{A0}/C_A)} = -\frac{1}{k_2} + \frac{k_1}{k_2}\left(\frac{t}{\ln (C_{A0}/C_A)}\right)$$

- hence

$$\frac{\ln (C_{A0}/C_A)}{C_{A0} - C_A} = -k_2 + \frac{k_1 t}{C_{A0} - C_A}$$

Continued…

- The rate form of shifting order reaction and some of its generalizations are used to represent a number of widely different kinds of reactions.
- For example, in homogeneous systems this form is used for enzyme-catalyzed reactions where it is suggested by mechanistic studies.
- It is also used to represent the kinetics of surface-catalyzed reactions.
- In mechanistic studies, this form of equation appears whenever the rate-controlling step of a reaction is viewed to involve the association of reactant with some quantity that is present in limited but fixed amounts; for example, the association of reactant with enzyme to form a complex, or the association of gaseous reactant with an active site on the catalyst surface.

Differential Method of Analysis of Data

- The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative dC_i/dt, and testing the goodness of fit of the equation with experiment. The procedure is as follows.

1. Plot the C_A vs. t data, and then by eye carefully draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.
2. Determine the slope of this curve at suitably selected concentration values. These slopes $dC_i/dt = r_A$ are the rates of reaction at these compositions.
3. Now search for a rate expression to represent this r_A vs. C_A data, either by (a) picking and testing a particular rate form, $-r_A = kf(C_A)$, (b) testing an nth-order form $-r_A = k(C_A)^n$: by taking logarithms of the rate equation

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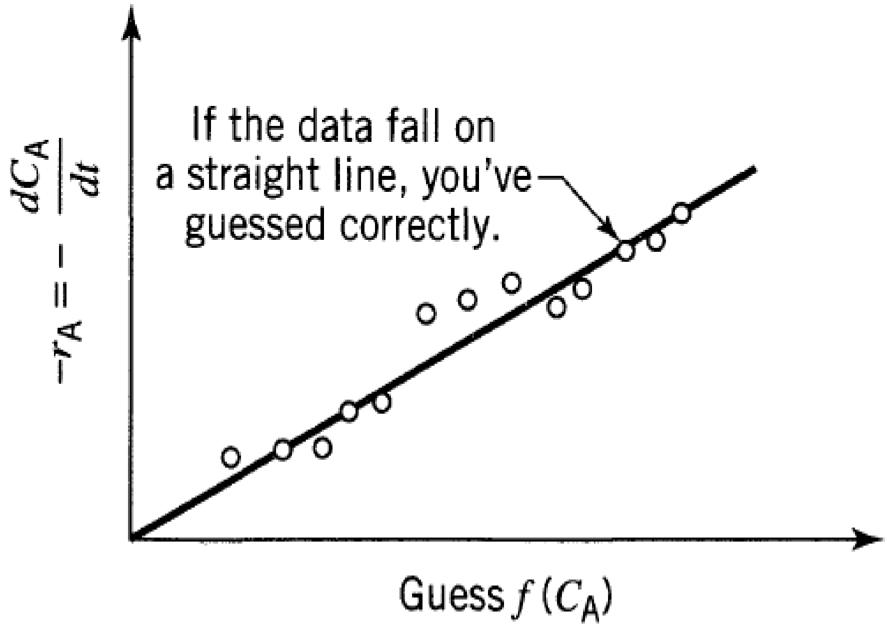


Fig: Test for the particular rate by the differential method

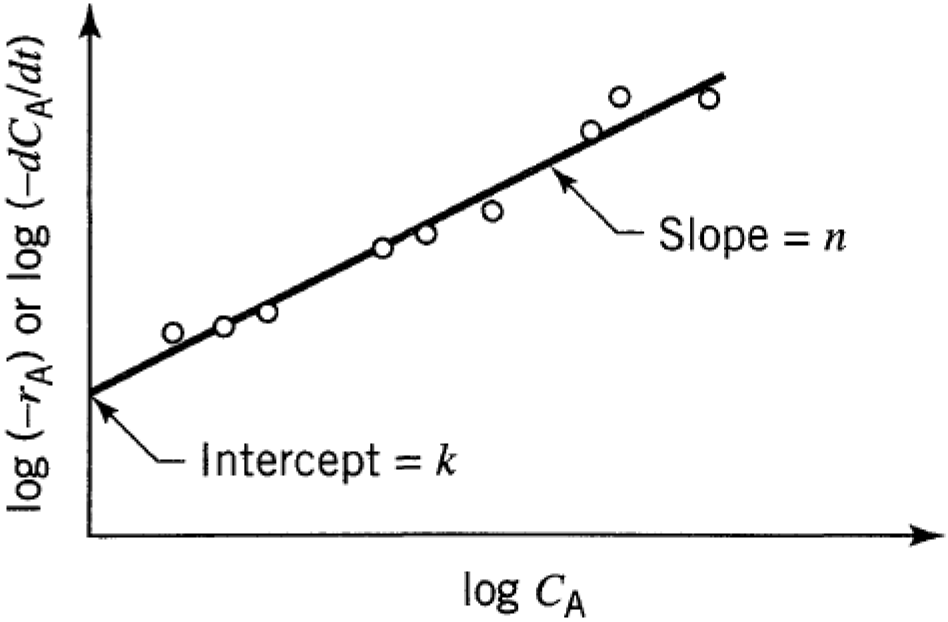
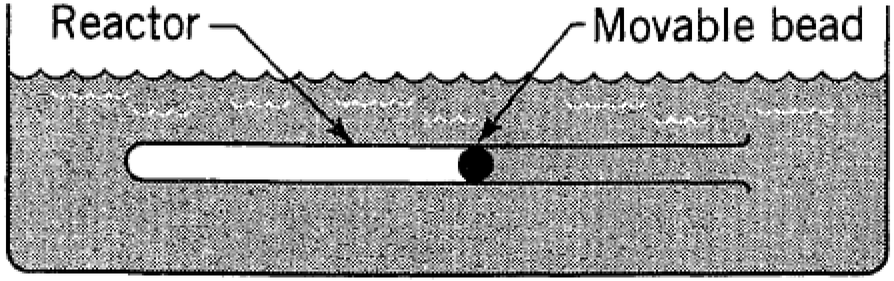


Fig: Test for the n-th order rate by the differential method

VARYING-VOLUME BATCH REACTOR

- These reactors are much more complex than the simple constant-volume batch reactor. Their main use would be in the micro-processing field where a capillary tube with a movable bead would represent the reactor (see Fig.). The progress of the reaction is followed by noting the movement of the bead with time, a much simpler procedure than trying to measure the composition of the mixture, especially for micro-reactors. Thus,



A varying-volume batch reactor

- V_0 = initial volume of the reactor
- V = the volume at time t.
- This kind of reactor can be used for isothermal constant pressure operations, of reactions having a single stoichiometry. For such systems the volume is linearly related to the conversion, or

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{or} \quad X_A = \frac{V - V_0}{V_0 \varepsilon_A} \qquad \text{hence} \qquad dX_A = \frac{dV}{V_0 \varepsilon_A}$$

Continued…

- where $\boldsymbol{\varepsilon}_A$ is the fractional change in volume of the system between no conversion and complete conversion of reactant A. Thus

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

- As an example of the use of $\boldsymbol{\varepsilon}_A$, consider the isothermal gas-phase reaction

$$\mathrm{A} \rightarrow 4\mathrm{R}$$

- By starting with pure reactant A,

$$\varepsilon_A = \frac{4-1}{1} = 3$$

- But with 50% inerts present at the start, two volumes of reactant mixture yield, on complete conversion, five volumes of product mixture. In this case

$$\varepsilon_A = \frac{5-2}{2} = 1.5$$

Continued…

- The ε_A accounts for both the reaction stoichiometry and the presence of inerts. Noting that

$$N_A = N_{A0}(1 - X_A)$$

- Therefore

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)} = C_{A0}\frac{1 - X_A}{1 + \varepsilon_A X_A}$$

- Hence $\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}$ and $X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}}$

- **This is the relationship between conversion and concentration for isothermal varying-volume (or varying-density) systems satisfying the linearity assumption**.

References

1. H. Scott Fogler, **Elements of Chemical Reaction Engineering**, Prentice Hall, 4th edition, 2005.
2. Octave Levenspiel, **Chemical Reaction Engineering**, John Wiley & Sons, 3rd edition, 1999.
3. Mark E. Davis, Robert J. Davis, **Fundamental of Chemical Reaction Engineering**, McGraw Hill, 1st edition, 2003.
4. Schmidt. Lanny D. **The Engineering of Chemical Reactions** Oxford University Press, Inc., New York, NY (1998).