BT209

Bioreaction Engineering

02/02/2023

$$\alpha A + \beta B + \cdots \rightarrow \text{products} \qquad \text{(present in stoichiometric ratio)}$$

we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \cdots$$

If the reactants are present in their stoichiometric ratios, they will remain at that ratio throughout the reaction. Thus, for reactants A and B at any time $C_B/C_A = \beta/\alpha$, and we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a \left(\frac{\beta}{\alpha} C_A\right)^b \cdots = k \underbrace{\left(\frac{\beta}{\alpha}\right)^b \cdots}_{\tilde{k}} \underbrace{C_A^{a+b+\cdots}}_{C_A^n}$$

or

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n$$

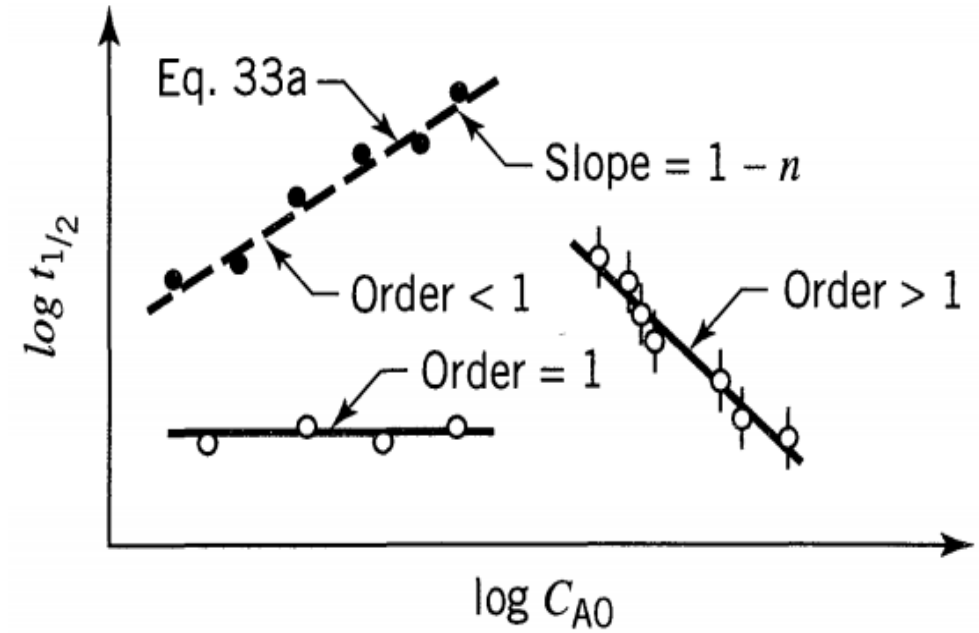Integrating for $n \neq 1$ gives

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

Defining the half-life of the reaction, $t_{1/2}$, as the time needed for the concentration of reactants to drop to one-half the original value, we obtain

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

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

The half-life method requires making a series of runs, each at a different initial concentration, and shows that the fractional conversion in a given time rises with increased concentration for orders greater than one, drops with increased

▪The half-life method can be extended to any fractional life method in which the concentration of reactant drops to any fractional value $F = C_A/C_{A0}$ in time t_F.

▪The derivation is a direct extension of the half-life method giving

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

Thus, a plot of log t_F versus log C_{A0}, will give the reaction order

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 $dC_A/dt = r_A$ are the rates of reaction at these compositions.
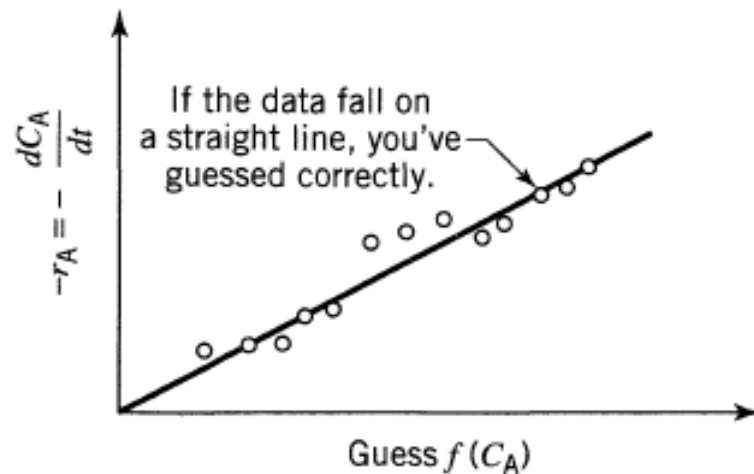

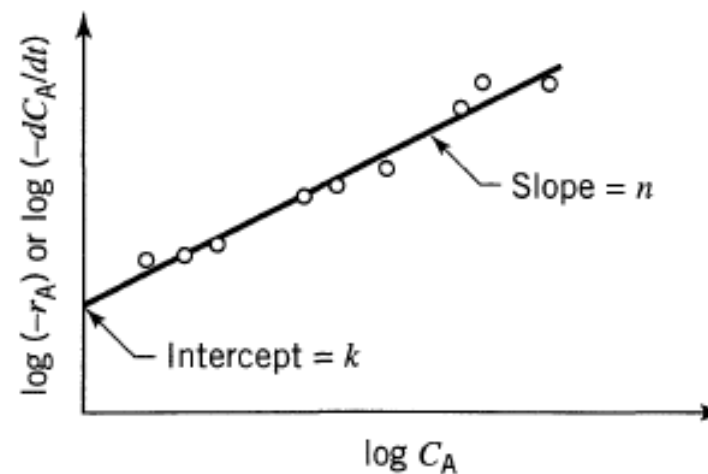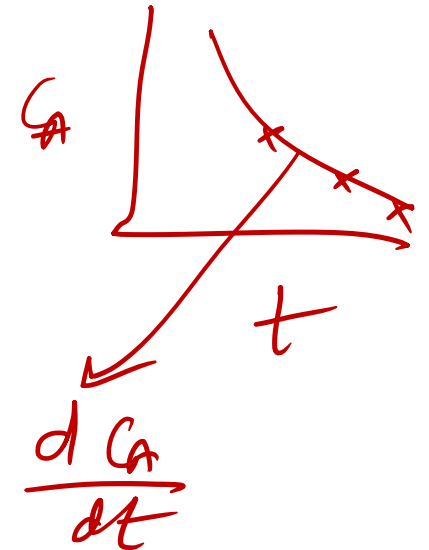**Figure 3.17** Test for the particular rate form $-r_A = kf(C_A)$ by the differential method.

Figure 3.18 Test for an *n*th-order rate form 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 microprocessing field where a capillary tube with a movable bead would represent the reactor

▪ 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 microreactors.

➢This kind of reactor can be used for isothermal constant pressure operations, of reactions having a single stoichiometry.
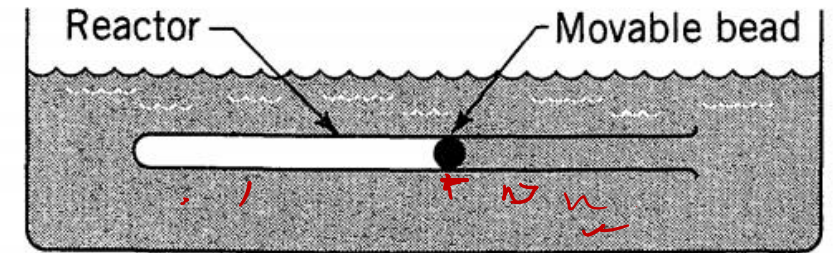
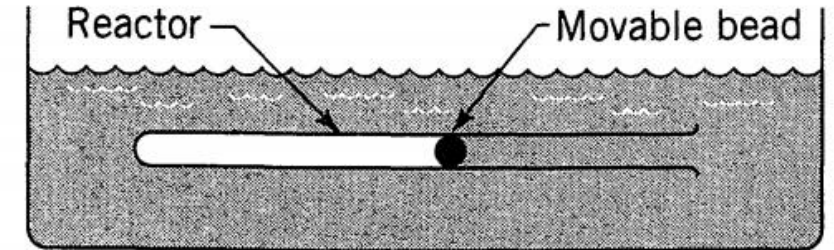V_0 = initial volume of the reactor
V = the volume at time t.

Cont.

➢ For such systems the volume is linearly related to the conversion

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

$$dX_A = \frac{dV}{V_0 \varepsilon_A}$$

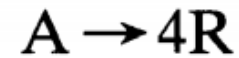$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

V_0 = initial volume of the reactor

V = the volume at time t.

where ε_A is the fractional change in volume of the system between no conversion and complete conversion of reactant A.

Reactor — Movable bead

As an example of the use of ε_A, consider the isothermal gas-phase reaction

$$A \longrightarrow 4R$$

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

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

➢ ε_A accounts for both the reaction stoichiometry and the presence of inerts

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

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

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} \quad \text{or} \quad X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}}$$

The rate of reaction (disappearance of component A), is, in general

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt}$$

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

varyus $\longrightarrow$ $C_A = C_{A0}\dfrac{1 - X_A}{1 + \varepsilon_A X_A}$

$$-r_A = \frac{C_{A0}}{(1 + \varepsilon_A X_A)}\frac{dX_A}{dt}$$

$$-r_A = \frac{C_{A0}}{V\varepsilon_A}\cdot\frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A}\cdot\frac{d(\ln V)}{dt}$$

$$\boxed{\begin{array}{c} dX_A = \dfrac{dV}{V_0\varepsilon_A} \\[2mm] V = V_0(1 + \varepsilon_A X_A) \end{array}}$$

❏For a homogeneous zero-order reaction the rate of change of any reactant A is independent of the concentration of materials, or

$$-r_A = \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = k$$

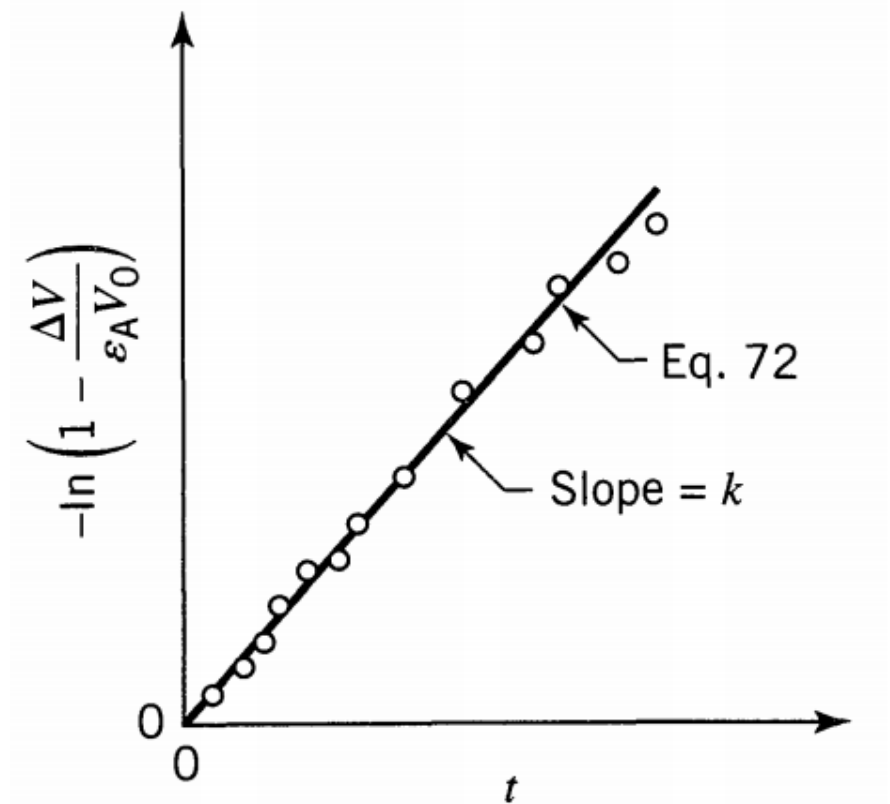$$\boxed{\frac{C_{A0}}{\varepsilon_A} \ln \frac{V}{V_0} = kt}$$
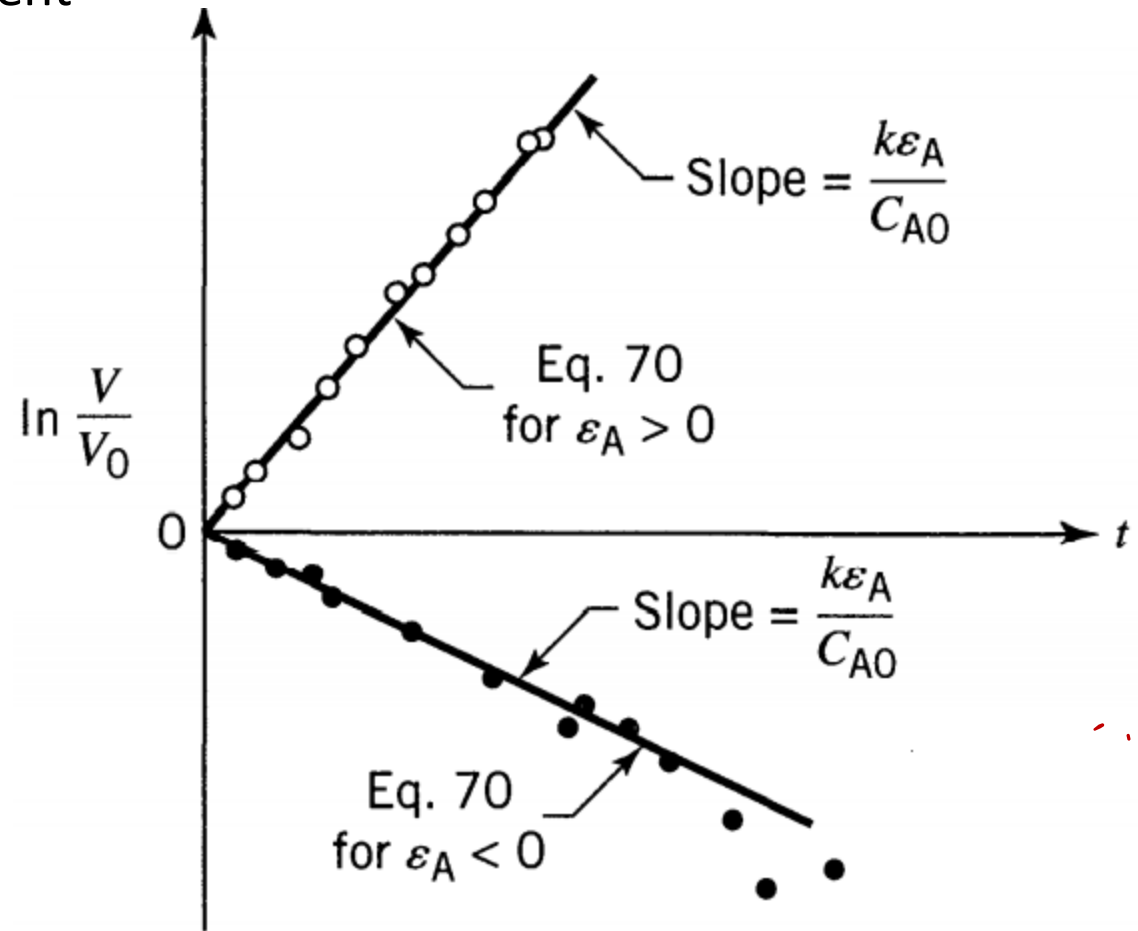
For a unimolecular-type first-order reaction the rate of change of reactant A is

$$-r_A = \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = kC_A = kC_{A0} \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right)$$

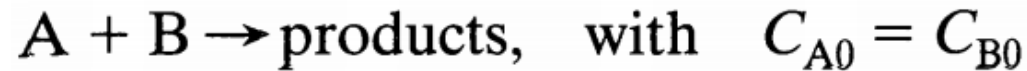$$-\ln\left(1 - \frac{\Delta V}{\varepsilon_A V_0}\right) = kt, \quad \Delta V = V - V_0$$

Eq. 72

Slope = k

For a bimolecular-type second-order reaction

$$2A \rightarrow \text{products}$$

Or

$$A + B \rightarrow \text{products}, \quad \text{with} \quad C_{A0} = C_{B0}$$

$$-r_A = \frac{C_{A0}}{\varepsilon_A} \frac{d \ln V}{dt} = kC_A^2 = kC_{A0}^2 \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right)^2$$

Replacing X_A by V and then integrating gives

$$\boxed{\frac{(1 + \varepsilon_A) \Delta V}{V_0 \varepsilon_A - \Delta V} + \varepsilon_A \ln \left(1 - \frac{\Delta V}{V_0 \varepsilon_A} \right) = kC_{A0}t}$$

Eq. 73

Slope = kC_{A0}