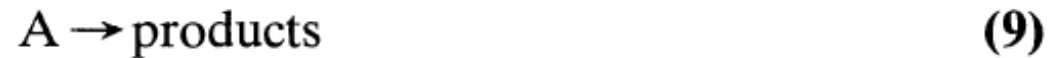


Irreversible Unimolecular-Type First-Order Reactions. Consider the reaction

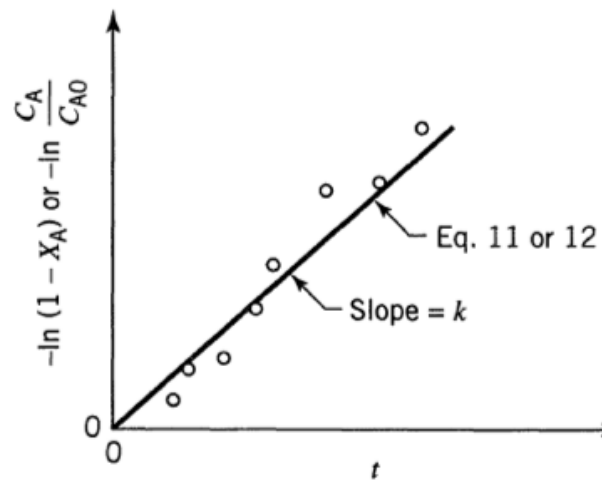


Suppose we wish to test the first-order rate equation of the following type,

$$-r_A = -\frac{dC_A}{dt} = kC_A \quad (10)$$

$$-\ln(1 - X_A) = kt$$

(12)



First order reaction solution

$$-r_i = k * C_i$$

$$-r_i = k * C_{i0} * (1-X)$$

$$-r_i = k * (C_{i0} + v_i \xi / V) \quad (V = \text{volume of reaction mixture})$$

$$C_i = C_{i0} * e^{-kt}$$

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

$$\xi = VC_{i0} / v_i * (-1 + e^{-kt})$$

What about other reaction rate equations?

Irreversible 2nd order, bimolecular elementary reaction

$2A \rightarrow \text{products}$

[initial concentration C_{A0} at $t = 0$]

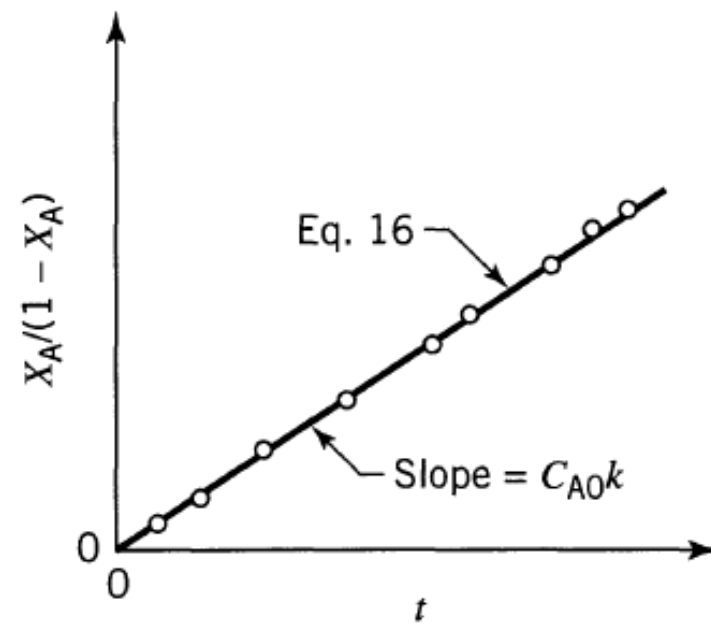
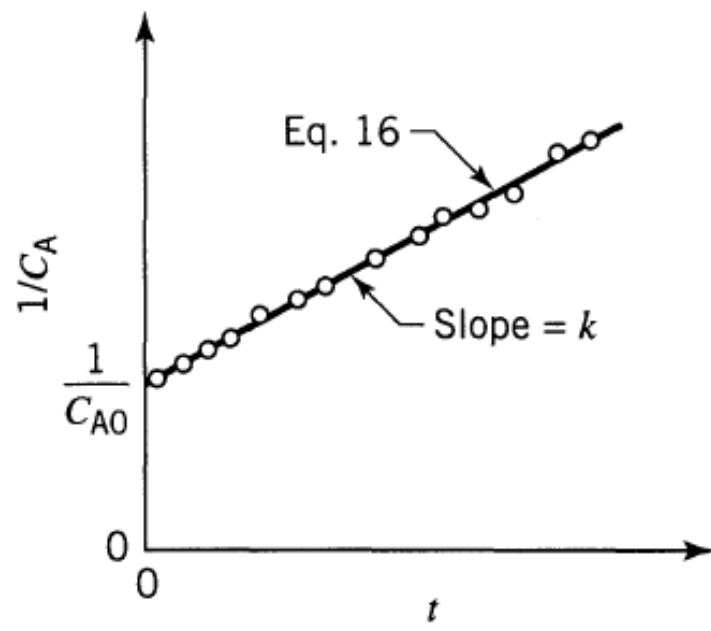
the defining second-order differential equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2 (1 - X_A)^2 \quad (15b)$$

which on integration yields

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = kt} \quad (16)$$

Note that this result is very different that the 1st order model, even though the only reactant is A. The order of the reaction is very important in obtaining the correct model.



2nd order, bimolecular elementary reaction
 $A + B \rightarrow \text{products}$

with corresponding rate equation

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \quad (13b)$$

[initial concentrations C_{A0} , C_{B0} at $t = 0$]

Noting that the amounts of A and B that have reacted at any time t are equal and given by $C_{A0}X_A$, we may write Eqs. 13a and b in terms of X_A as

$$-r_A = C_{A0} \frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

Letting $M = C_{B0}/C_{A0}$ be the initial molar ratio of reactants, we obtain

$$-r_A = C_{A0} \frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A)$$

which on separation and formal integration becomes

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0}k \int_0^t dt$$

After breakdown into partial fractions, integration, and rearrangement, the final result in a number of different forms is

$$\boxed{\begin{aligned} \ln \frac{1 - X_B}{1 - X_A} &= \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{C_B}{M C_A} \\ &= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \quad M \neq 1 \end{aligned}} \quad (14)$$

note that this is only valid for $C_{A0} \neq C_{B0}$

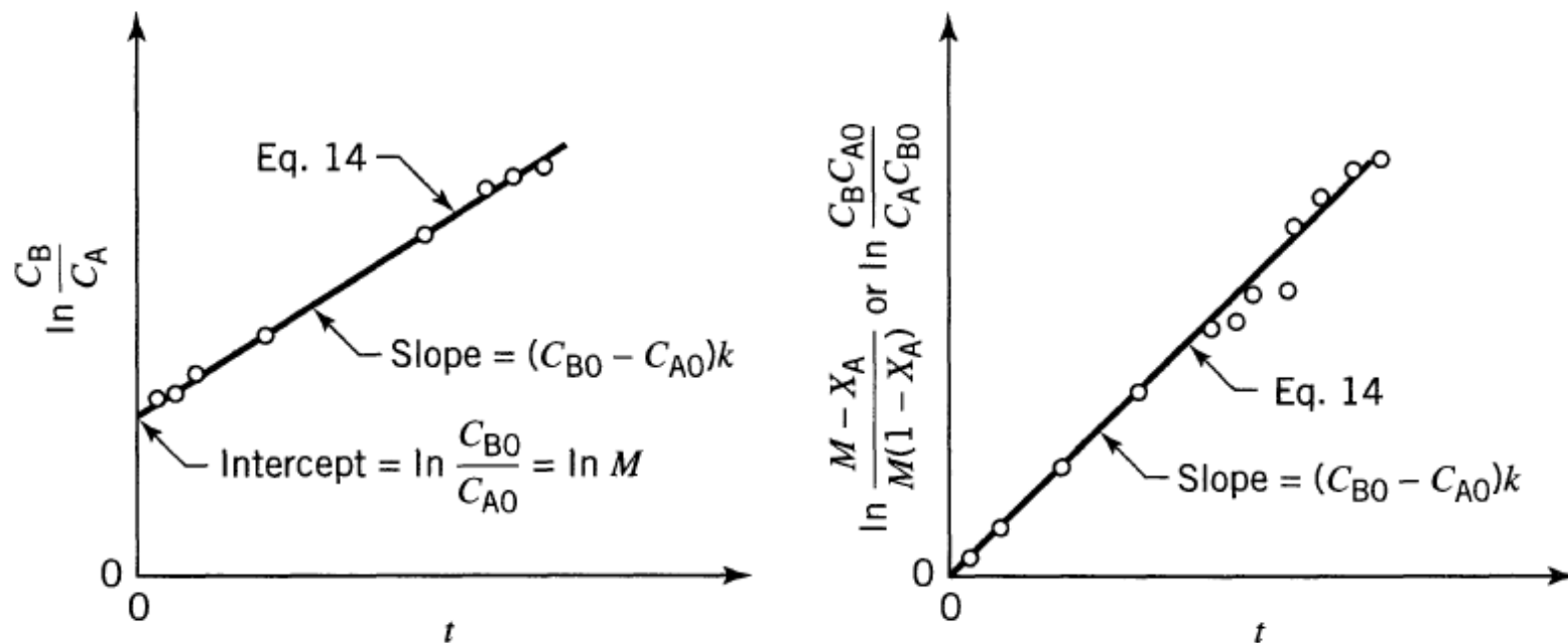


Figure 3.2 Test for the bimolecular mechanism $A + B \rightarrow R$ with $C_{A0} \neq C_{B0}$, or for the second-order reaction, Eq. 13.



is first order with respect to both A and B, hence second order overall, or

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B = kC_{A0}^2 (1 - X_A)(M - 2X_A) \quad (17b)$$

The integrated form is

$$\ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{M - 2X_A}{M(1 - X_A)} = C_{A0}(M - 2)kt, \quad M \neq 2 \quad (18)$$

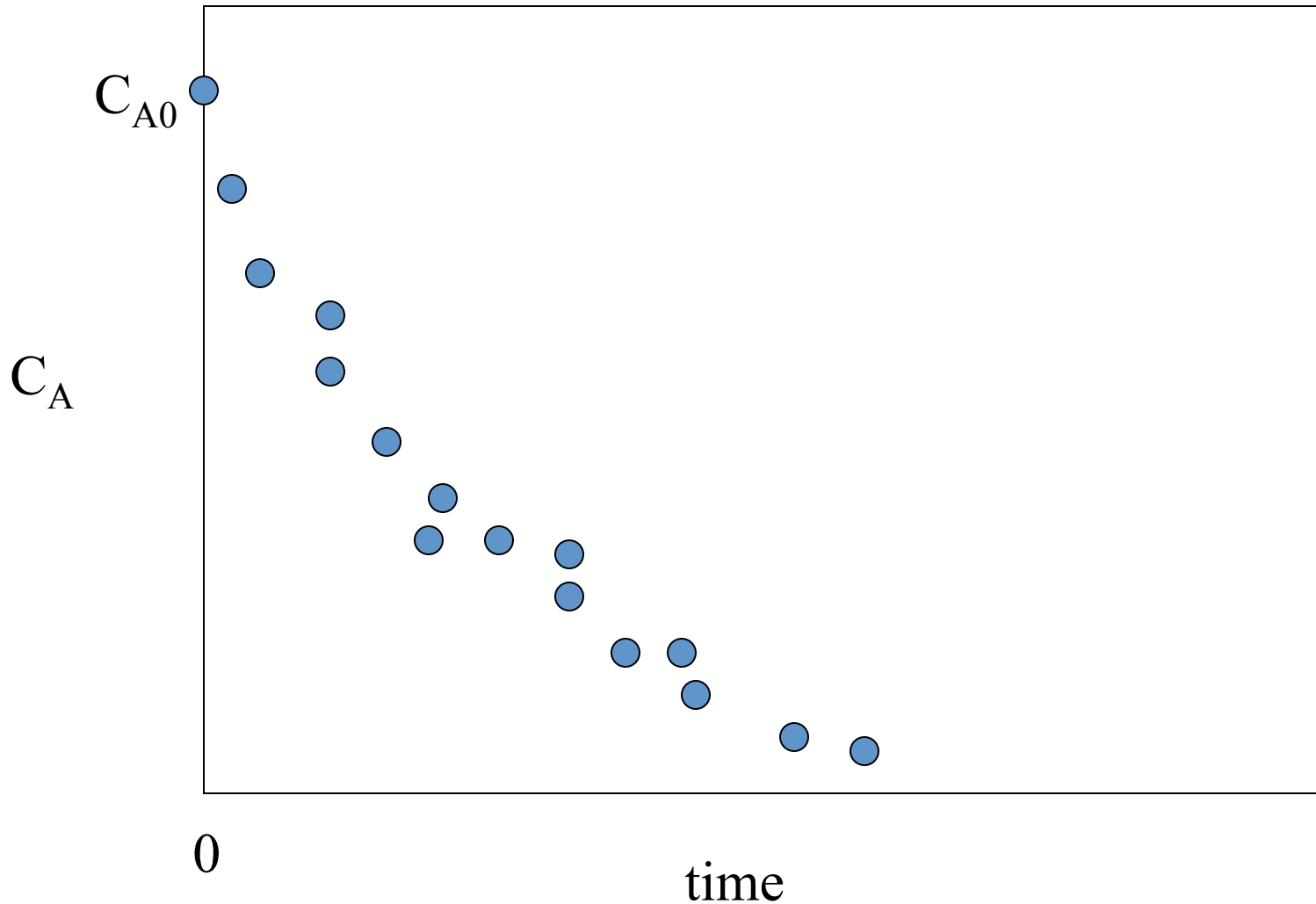
When a stoichiometric reactant ratio is used the integrated form is

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2kt, \quad M = 2 \quad (19)$$

The integrated expression depends on the stoichiometry as well as the kinetics!

Assume you have measured the concentration of some reactant A vs. time in a fixed volume batch reactor at constant temperature.

How can you use this data to establish a reaction rate model?



Integral rate data analysis (develop model, see if it fits data)

Let's assume an elementary, first order, unimolecular decomposition model,



the reaction rate equation for this model would be:

$$-r_A = -dC_A/dt = k \cdot C_A$$

with the initial condition that $C_A = C_{A0}$ at $t = 0$

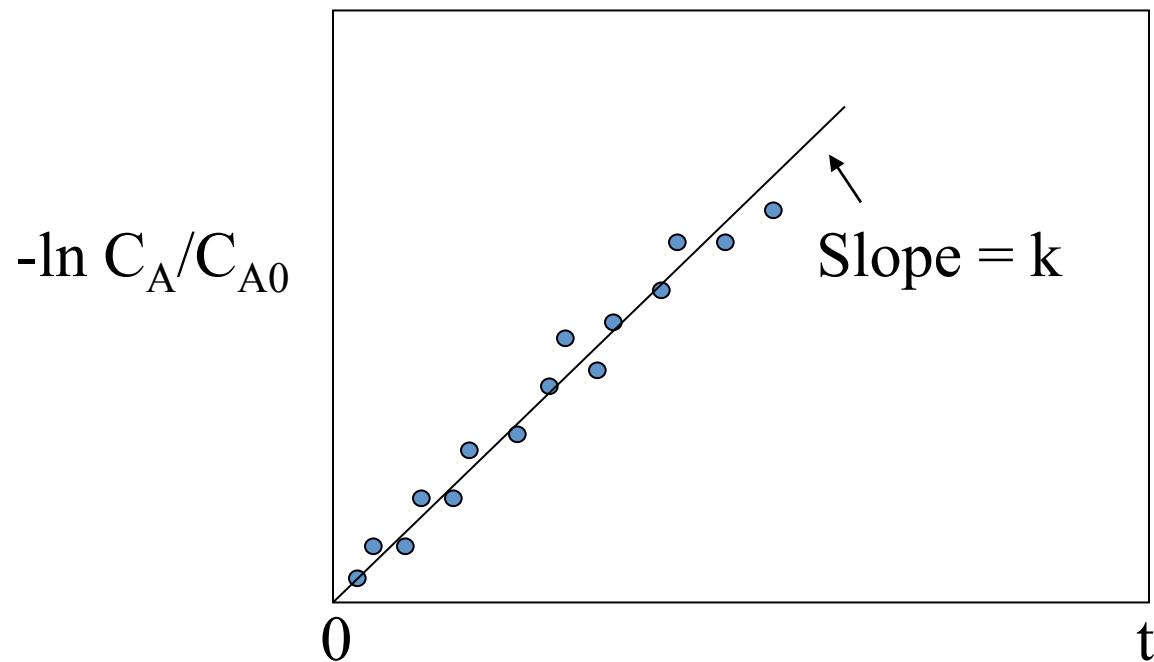
Integrating this equation by simply separating variables yields:

$$\begin{aligned} -r_A &= -dC_A/dt = k \cdot C_A \\ -\int dC_A / C_A &= \int k dt \end{aligned}$$

$$-\ln (C_A / C_{A0}) = kt$$

Note that this is a unimolecular reaction, so A basically decomposes into products

Plotting the data values as $-\ln (C_A/ C_{A0})$ vs. t would show a straight line through the data, whose statistical goodness of fit would indicate the validity of the model



The basic idea behind rate data analysis using the integral method is to:

1. Setup a rate equation based on a hypothesized elementary reaction model
2. Integrate the model to obtain $f(C) = kt$
3. Examine the plot of $f(C)$ vs. t with the data for linearity, which would indicate a valid reaction model