Fractional Conversion

$f_i = \frac{(N_{i,0} - N_i)}{N_{i,0}}$, Ni = number of moles present; Ni0 = number of moles initially present

Extent of Reaction

$\xi = \frac{(N_i - N_{i,0})}{v_i}$, vi = stoichiometric coefficient of balance eqn (negative for reactants)

General form of component material balance for species i

$\sum x_{ij} * Q_j + \sum \xi * v_i = 0$, Xij = mole fraction of i in stream j; Qj = molar flowrate of stream j

$\sum \omega_{ij} * F_j + \sum \xi * v_i * MW_i = 0$, Wij = mass fraction, Fj = mass flowrate, MWi = molecular weight
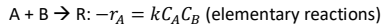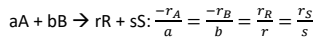
Conversion

$X = \frac{(C_0 - C)}{C_0} = 1 - \frac{C}{C_0}$

General Rate of Reaction

$r_i = \frac{1}{V} * \frac{dN_i}{dt}$, ri = reaction rate, V = volume, Ni = moles of i, t = time

aA + bB → rR + sS: $\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$

A + B → R: $-r_A = kC_AC_B$ (elementary reactions)

Arrhenius' Law

$k = k_0 e^{\frac{-E}{R*T}}$, k0 = pre-exponential factor, E = activation energy

$\ln\left(\frac{r_2}{r_1}\right) = \ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$, R = 8.314 J/mol.K

Constant-Volume Batch Reactor Assumption:

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

Conversion

$X_A = \frac{N_{A,0} - N_A}{N_{A,0}} = 1 - \frac{\frac{N_A}{V}}{\frac{N_{A,0}}{V}} = 1 - \frac{C_A}{C_{A,0}}$, $dX_A = \frac{-dC_A}{C_{A,0}}$

Separating and Integrating

$-\int_{C_{A,0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt$, $-\ln\frac{C_A}{C_{A,0}} = kt$; $\int_0^{X_A}\frac{dX_A}{1-X_A} = k\int_0^t dt$, $-\ln(1-X_A) = kt$

First Order Reaction Solution

$-r_i = k*C_i = k*C_{i,0}*(1-X) = k*(C_{i,0} + \frac{v_i\xi}{V})$; $C_i = C_{i,0}*e^{-kt}$; $X = 1 - e^{-kt}$; $\xi = \frac{V*C_{i,0}}{v_i*(-1+e^{-kt})}$

Irreversible Second Order (2A → Products)

$-r_A = \frac{-dC_A}{dt} = kC_A^2 = kC_A^2(1-X_A)^2$; $\frac{1}{C_A} - \frac{1}{C_{A,0}} = \frac{1}{C_{A,0}}\frac{X_A}{1-X_A} = kt$

A + 2B → Products

$-r_A = \frac{-dC_A}{dt} = kC_AC_B = kC_{A0}^2(1-X_A)(M-2X_A)$; $\ln\frac{C_BC_{A,0}}{C_{B,0}C_A} = \ln\frac{M-2X_A}{M(1-X_A)} = C_{A,0}(M-2)kt$, $M \neq 2$

$\frac{1}{C_A} - \frac{1}{C_{A,0}} = \frac{1}{C_{A,0}}\frac{X_A}{1-X_A} = 2kt$, $M = 2$

Rate Data Analysis Using Integral Method

1. Set up rate equation based on hypothesized elementary reaction model
2. Integrate model to get f(C)=kt
3. Examine plot of f(C) vs. t with data for linearity, which indicates valid reaction model

Irreversible Trimolecular-Type Third-Order Reactions (A + B + D → Products)

$-r_A = \frac{-d_A}{dt} = kC_AC_BC_D$; $C_{A,0}\frac{dX_A}{dt} = kC_{A,0}^3(1-X_A)(\frac{C_{B,0}}{C_{A,0}} - X_A)(\frac{C_{D,0}}{C_{A,0}} - X_A)$

$\frac{1}{(C_{A,0}-C_{B,0})(C_{A,0}-C_{D,0})}\ln\frac{C_{A,0}}{C_A} + \frac{1}{(C_{B,0}-C_{D,0})(C_{B,0}-C_{A,0})}\ln\frac{C_{B,0}}{C_B} + \frac{1}{(C_{D,0}-C_{A,0})(C_{D,0}-C_{B,0})}\ln\frac{C_{D,0}}{C_D} = kt$

Assuming CD0 is much larger than both CA0 and CB0, M = CB0/CA0:

$\ln\frac{1-X_B}{1-X_A} = \ln\frac{M-X_A}{M(1-X_A)} = \ln\frac{C_BC_{A,0}}{C_{B,0}C_A} = \ln\frac{C_B}{MC_A} = C_{A,0}(M-1)kt = (C_{B,0} - C_{A,0})kt$, $M \neq 1$

Empirical Rate Equations of nth Order:

$C_n^{1-n} - C_{A,0}^{1-n} = (n-1)kt$, $n \neq 1$

Zero-Order Reactions

$-r_A = \frac{-dC_A}{dt} = k$; $C_{A,0} - C_A = C_{A,0}X_A = kt$ for $t < \frac{C_{A,0}}{k}$; $C_A = 0$ for $t \geq \frac{C_{A,0}}{k}$

Parallel Reactions (A → R, A → S):

$-r_A = \frac{-dC_A}{dt} = k_1C_A + k_2C_A = (k_1 + k_2)C_A$; $r_R = \frac{dC_R}{dt} = k_1C_A$; $r_S = \frac{dC_S}{dt} = k_2C_A$

$-\ln\frac{C_A}{C_{A,0}} = (k_1 + k_2)t$; $\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$; $\frac{C_R - C_{R,0}}{C_S - C_{S,0}} = \frac{k_1}{k_2}$ ←know k1 + k2 and k1*k2... solve for both; higher k = higher ending concentration

Linearized Regression for Fitting Functions to Data

First Order: $f(C) = \ln\frac{C}{C_0}$; Second Order: $f(C) = \frac{1}{C} - \frac{1}{C_0}$; Third Order: $f(C) = \frac{1}{C^2} - \frac{1}{C_0^2}$

Select a rate equation, f(C), plot dC/dt vs. f(C) and evaluate for goodness of fit (slope = k)

Nth Order Rate Models

1. Fit data to curve C(t)
2. Take derivatives, dC/dt
3. Plot log of -dC/dt vs. log C(t) and fit to line ln(-dC/dt) = lnk + n*lnC
4. Slope = n, exp(intercept) = k

Deriving Mechanistic Rate Equation Models

1. Propose a mechanism composed of elementary reactions
2. Determine how many components/species are present in reactions
3. Make assumptions regarding transition species behavior (dx/dt = 0, [x] = constant, etc)
4. Algebraically solve for transition species concentrations and solve for measurable species rate equations
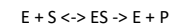5. Simplify/make assumptions to see if rate equations fit observed behavior

Elementary Reaction: -vaA – vbB → Products:

$r_A = -kC_A^{-v_A}C_B^{-v_B}$; $r_B = \frac{v_B}{v_A}*r_A = -(\frac{v_B}{v_A})kC_A^{-v_A}C_B^{-v_B}$

Michealis-Menton Equation:

$\frac{d[S]}{dt} = \frac{A*[S]}{(B+[S])}$

Derivation:

E + S <-> ES -> E + P

$k_1[E][S] = k_{-1}[ES]$; $\frac{[E][S]}{[ES]} = \frac{k_{-1}}{k_1} = K_S$; $[E] = [E_0] - [ES]$; $\frac{([E_0]-[ES])[S]}{[ES]} = K_S$; $[ES] = \frac{[E_0][S]}{(K_S + [S])}$

$v = k_2[ES] = \frac{K_S[E_0][S]}{K_S + [S]} = \frac{V_m[S]}{K_m + [S]} = \frac{-d[S]}{dt} = \frac{d[P]}{dt}$; $V_m = k_2[E_0]$; $K_m = K_S$

Briggs-Haldane Analysis

$k_1[E][S] = (k_{-1} + k_2)[ES]$; $[ES] = \frac{k_1[E][S]}{k_{-1}+k_2}$; $[E] = [E_0] - [ES]$; $[ES] = \frac{[E_0][S]}{\left(\frac{k_{-1}+k_2}{k_1}+[S]\right)} = \frac{[E_0][S]}{(K_m+[S])}$

$v = k_2[ES] = \frac{k_2[E_0][S]}{(K_m + [S])} = \frac{V_m[S]}{(K_m + [S])}$

Km values:

Low Km means that the enzyme binds strongly to the substrate; high km means enzyme prefers to release; range of 10^-2 to 10^-6

When km >> [S], first order reaction; when [S] >> km, zero order reaction

Kcat

$V_m = k_{cat}[E_0]$; kcat = turnover number, max rate of substrate conversion per enzyme molecule

$\frac{k_{cat}}{K_m} = \eta$; catalytic efficiency (reaction rate/binding affinity)

Linearized Models

Lineweaver-Burke

$\frac{1}{v} = \left(\frac{K_m}{V_m}\right)\left(\frac{1}{[S]}\right) + \frac{1}{V_m}$; limitations: overly sensitive at low [S], need large [S] near 1/Vm

Eadie-Hofstee Linear Plot

$v = -K_m\left(\frac{v}{[S]}\right) + V_m$; limitations: overly sensitive at low [S]

Hanes Linearized Plot

$\frac{[S]}{v} = \frac{1}{V_m} * [S] + \frac{K_m}{V_m}$; limitations: sensitivity at low v

When Ca = Cm, half enzyme free, half combined; Ca >> Cm, zero order; Ca << Cm, first order

Integrated M-M equation

$C_M \ln\frac{C_{A,0}}{C_A} + (C_{A,0} - C_A) = k_3 C_{E,0}t$; first order at low Ca, shift at Ca = cm, zero order at high Ca

$\frac{C_{A,0}-C_A}{\ln\frac{C_{A,0}}{C_A}} = -C_M + k_3 C_{E,0}\frac{t}{\ln\frac{C_{A,0}}{C_A}}$
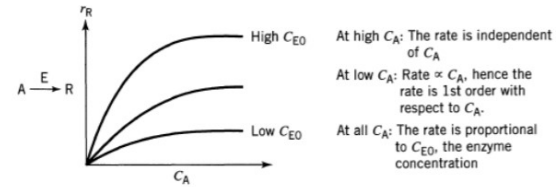

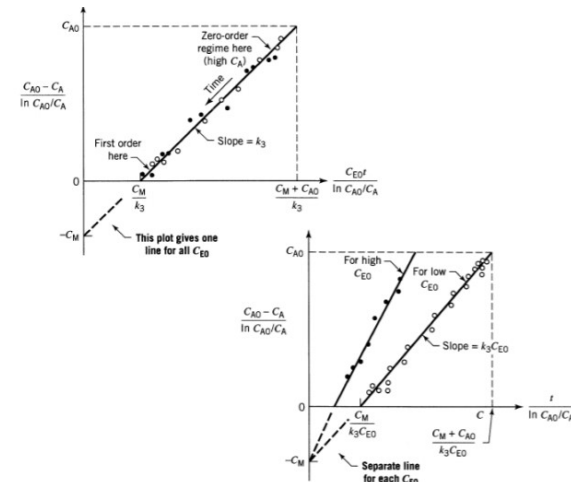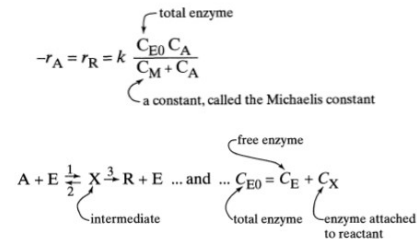**Figure 27.2** Typical rate-concentration curves for enzyme catalyzed reactions.

Figure 27.5 Either plot can be used to test and fit the M–M equation (Eq. 6) from batch reactor data.