BT209

Bioreaction Engineering

18/01/2023

Temperature dependent term of rate equation

For many reactions, the rate expression can be written as a product of a temperature-dependent term and a concentration dependent term

$$r_i = f_1(\text{Temperature}) \cdot f_2(\text{Concentration})$$
$$= k \cdot f_2(\text{Concentration})$$

For such reactions the temperature-dependent term, the reaction rate constant, has been found in practically all cases to be well represented by **Arrhenius' law**:

$$k = k_0 T^m \, e^{-\frac{E}{RT}}$$

$0 \leq m \leq 1$

Based on collision (m=0.5) and transition state theory (m=1)

k_0 is called the frequency or pre-exponential factor
E is called the activation energy

$$k = k_0 e^{-E/R T}$$ As exponential term much more sensitive
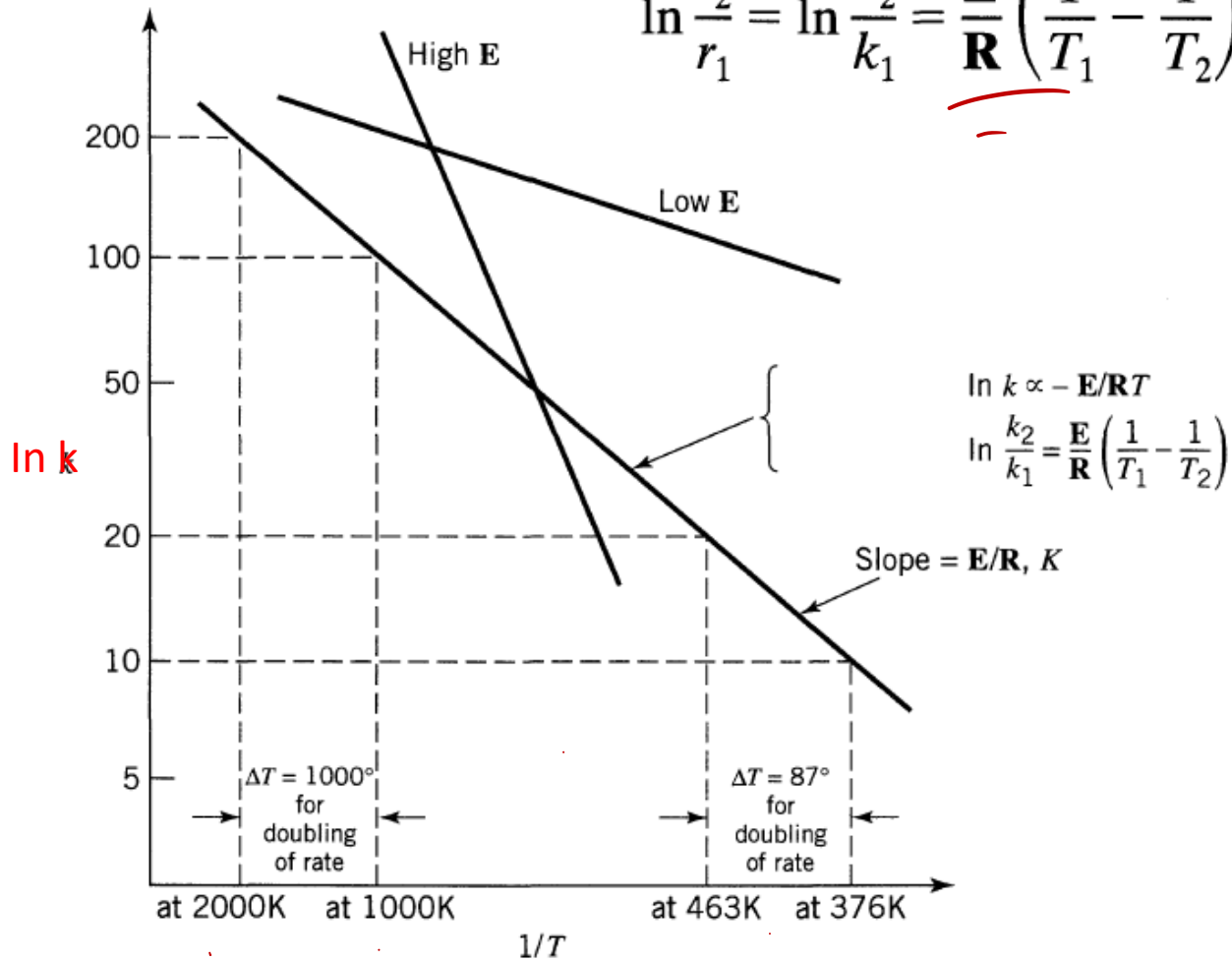
At the same concentration, but at two different temperatures, Arrhenius' law indicates that

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Temperature dependent term of rate equation

$$k = k_0 e^{-E/RT}$$

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

High E

Low E

$\ln k \propto - E/RT$

$\ln \frac{k_2}{k_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Slope = E/R, K

$\Delta T = 1000°$ for doubling of rate

$\Delta T = 87°$ for doubling of rate

In k

at 2000K   at 1000K   at 463K   at 376K

1/T

1. From Arrhenius' law a plot of In k vs 1/T gives a straight line, with large slope for large E and small slope for small E.

2. Reactions with high activation energies are very temperature-sensitive; reactions with low activation energies are relatively temperature-insensitive.

3. Any given reaction is much more temperature-sensitive at a low temperature than at a high temperature.

$$aA \quad + \quad bB \quad + \cdots = \quad rR \quad + \quad sS \quad + \cdots$$

➢Totally consumed when the chemical reaction is complete

Check: min {(N_{A0} available/a), (N_{B0} available/b),……………. }

➢Corresponding reactant is rate limiting reactant

CONSTANT-VOLUME BATCH REACTOR

When we mention the constant-volume batch reactor we are really referring 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.

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

or for ideal gases, where $C = p/\mathbf{R}T$,

$$r_i = \frac{1}{\mathbf{R}T}\frac{dp_i}{dt}$$

Thus, the rate of reaction of any component is given by the rate of change of its concentration or partial pressure; so no matter how we choose to follow the progress of the reaction, we must eventually relate this measure to the concentration or partial pressure if we are to follow the rate of reaction

Fractional Conversion

Reaction: aA+bB→cC+dD

- **Conversion**, $X_j = \dfrac{N_{j0} - N_j}{N_{j0}}$

N_{j0} : initial mole of jth reactant

N_j : Final mole of jth reactant

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

$$N_B = N_{B0}\left(1 - X_B\right)$$

At constant volume

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

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

$$C_A = C_{A0}\left(1 - X_A\right) = C_{A0} - C_{A0}X_A = \text{Inital A} - \text{Chagne of A}$$

- Two types:
  - ➢Integral method :

    Rate equation integration and compare C vs t data. If fit is unsatisfactory another rate expression is guessed and tested

  - ➢Differential method:

    Plot dC_A/dt vs t

Irreversible unimolecular type 1st order   A→P

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

$$\frac{dX_A}{dt} = k(1 - X_A)$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt$$

$$\int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

$$-\ln \frac{C_A}{C_{A0}} = kt$$

$$\boxed{-\ln (1 - X_A) = kt}$$
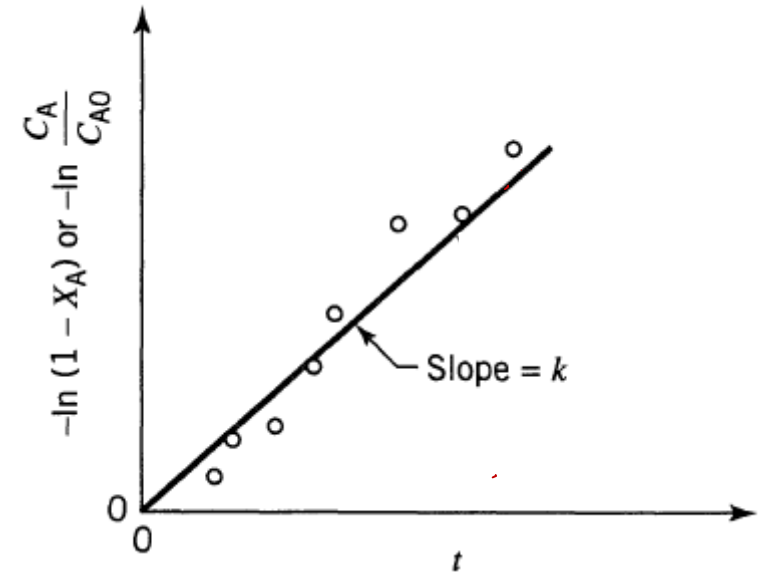
Caution. We should point out that equations such as

$$-\frac{dC_A}{dt} = kC_A^{0.6}C_B^{0.4}$$

are first order but are not amenable to this kind of analysis; hence, not all first-order reactions can be treated as shown above.
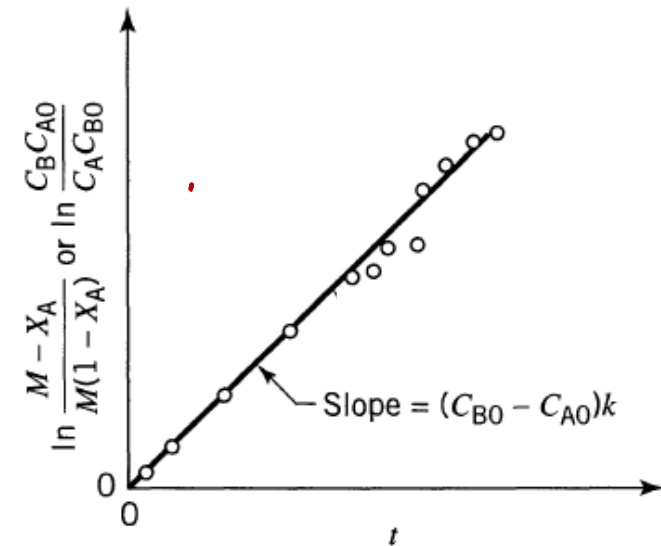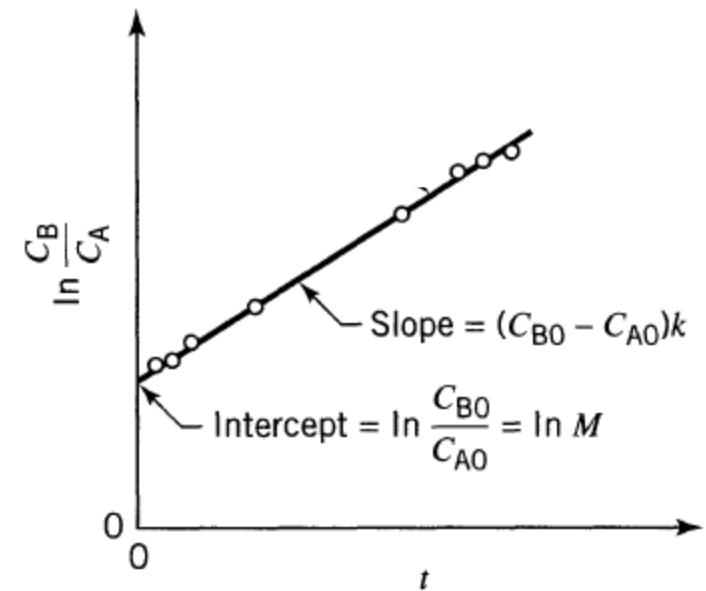
Consider, $A + B \rightarrow products$ with $-r_A = -\dfrac{dC_A}{dt} = -\dfrac{dC_B}{dt} = kC_AC_B$

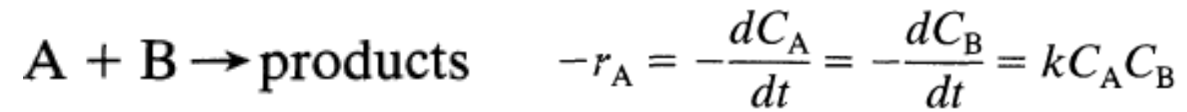$$-r_A = C_{A0}\frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

$$-r_A = C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A) \qquad M = C_{B0}/C_{A0}.$$

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

$$\ln\frac{1 - X_B}{1 - X_A} = \ln\frac{M - X_A}{M(1 - X_A)} = \ln\frac{C_BC_{A0}}{C_{B0}C_A} = \ln\frac{C_B}{MC_A}$$

$$= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \qquad M \neq 1$$

If C_{B0} is much larger than C_{A0}, C_B remains approximately constant at all times,

$$A + B \longrightarrow \text{products} \qquad -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B$$

1st order type

Thus, the second order reaction becomes a pseudo first-order reaction.

Zero-Order Reactions. A reaction is of zero order when the rate of reaction is independent of the concentration of materials; thus

$$-r_A = -\frac{dC_A}{dt} = k$$

Integrating and noting that C_A can never become negative, we obtain directly

$$C_{A0} - C_A = C_{A0}X_A = kt \quad \text{for} \quad t < \frac{C_{A0}}{k}$$

$$C_A = 0 \quad \text{for} \quad t \geq \frac{C_{A0}}{k}$$

which means that the conversion is proportional to time,