

University of Anbar

College of Engineering

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Department**

Chemical Reaciior Design

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Lecture No. 3

TEMPERATURE-DEPENDENT TERM OF A RATE EQUATION

Temperature Dependency from Arrhenius' Law

For many reactions, and particularly elementary reactions, the rate expression can be written as a product of a temperature-dependent term and a composition dependent term, or:

$$r_i = f_1(\text{temperature}) \cdot f_2(\text{composition}) = k \cdot f_2(\text{composition}) \quad (7)$$

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**:

$$k = k_0 e^{-E/RT} \quad (8)$$

where k_0 , is called the frequency or pre-exponential factor and E is called the activation energy of the reaction

At the same concentration, but at two different temperatures, Arrhenius' law indicates that:

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9)$$

The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction, as illustrated in Fig. 2.2

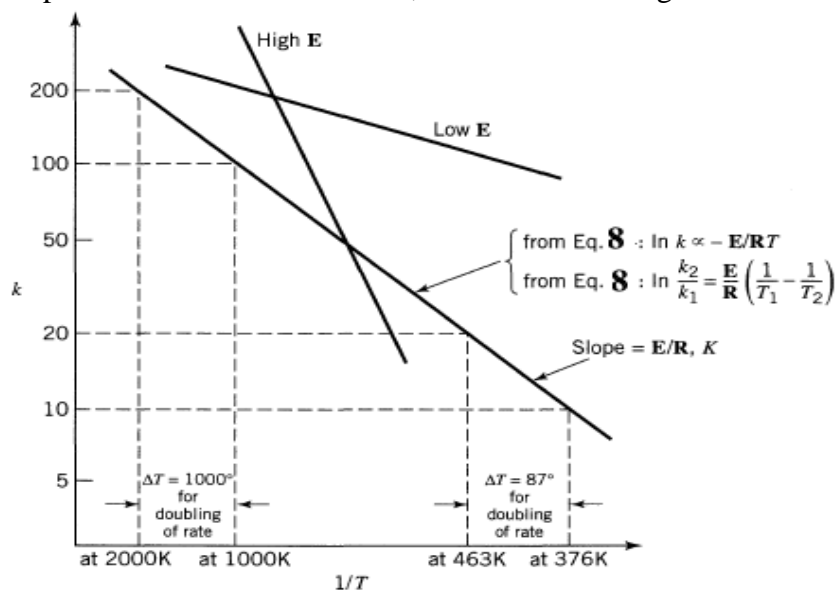


Figure 2.2 Sketch showing temperature dependency of the reaction rate.

These findings are summarized as follows:

1. From Arrhenius' law a plot of $\ln k$ 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.
4. From the Arrhenius law, the value of the frequency factor k_0 , does not affect the temperature sensitivity.

EXAMPLE 2. SEARCH FOR THE ACTIVATION ENERGY OF A PASTEURIZATION PROCESS

Milk is pasteurized if it is heated to 63°C for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy of this sterilization process.

SOLUTION

To ask for the activation energy of a process means assuming an Arrhenius temperature dependency for the process. Here we are told that

$$\begin{aligned}t_1 &= 30 \text{ min} & \text{at a } T_1 &= 336 \text{ K} \\t_2 &= 15 \text{ sec} & \text{at a } T_2 &= 347 \text{ K}\end{aligned}$$

Now the rate is inversely proportional to the reaction time, or rate $\propto 1/\text{time}$ so Eq. 35 becomes

$$\ln \frac{r_2}{r_1} = \ln \frac{t_1}{t_2} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or

$$\ln \frac{30}{0.25} = \frac{E}{8.314} \left(\frac{1}{336} - \frac{1}{347} \right)$$

from which the activation energy

$$\underline{E = 422\,000 \text{ J/mol}}$$

Interpretation of Batch Reactor Data:

There are two procedures for analyzing kinetic data, the **integral** and the **differential methods**.

- **In the integral method** of analysis after 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
- **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 $(1/V)(dN/dt)$ from the data before attempting the fitting procedure

CONSTANT-VOLUME BATCH REACTOR:

The constant-volume batch reactor we refer 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

$$\boxed{r_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{d(N_i/V)}{dt} = \frac{dC_i}{dt}} \quad (10)$$

or for ideal gases, where $C = P/RT$,

$$\boxed{r_i = \frac{1}{RT} \frac{dp_i}{dt}} \quad (11)$$

For gas reactions with changing numbers of moles, a simple way of finding the reaction rate is to follow the change in total pressure. π of the system.



Initially the total number of moles present in the system is

$$N_0 = N_{A0} + N_{B0} + \dots + N_{R0} + N_{S0} + \dots + N_{inert}$$

but at time t it is

$$N = N_0 + x(r + s + \dots - a - b - \dots) = N_0 + x \Delta n \quad (3)$$

where

$$\Delta n = r + s + \dots - a - b - \dots$$

Assuming that the ideal gas law holds, we may write for any reactant, say A in the system of volume V

$$C_A = \frac{p_A}{RT} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V} \quad (4)$$

Combining Eqs. 3 and 4 we obtain

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

or

$$\boxed{p_A = C_A RT = p_{A0} - \frac{a}{\Delta n} (\pi - \pi_0)} \quad (5)$$

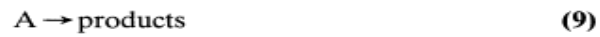
The Conversion:

Suppose that N_{A0} 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:

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A/V}{N_{A0}/V} = 1 - \frac{C_A}{C_{A0}} \quad (7) \quad dX_A = -\frac{dC_A}{C_{A0}}$$

Integral Method of Analysis of Data:

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



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

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

for this reaction. Separating and integrating we obtain

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

or

$$-\ln \frac{C_A}{C_{A0}} = kt \quad (11)$$

$$\frac{dX_A}{dt} = k(1 - X_A) \quad \longrightarrow \quad \int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

$$\boxed{-\ln(1 - X_A) = kt} \quad (12)$$

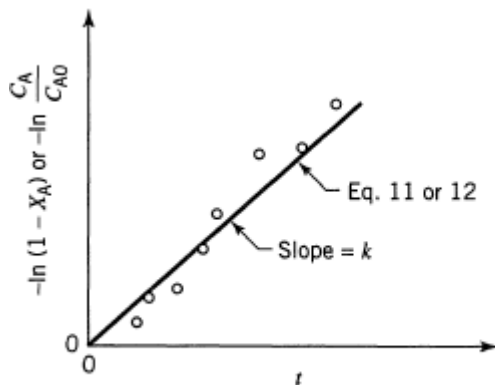


Figure 3.1 Test for the first-order rate equation, Eq. 10.

Irreversible Bimolecular-Type Second-Order Reactions. Consider the reaction:



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

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

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

Figure 3.2 shows two equivalent ways of obtaining a linear plot between the concentration function and time for this second-order rate law.

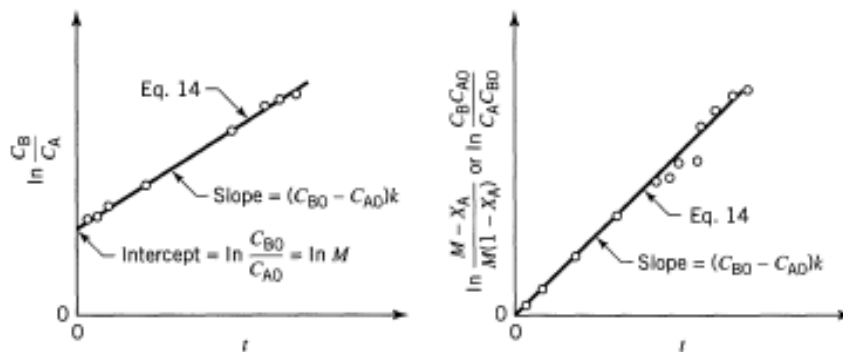


Figure 3.2 Test for the bimolecular mechanism $A + B \rightarrow R$ with $C_{A0} \neq C_{B0}$, or for the second-order reaction, Eq. 13.

Caution 1. In the special case where reactants are introduced in their stoichiometric ratio, the integrated rate expression becomes indeterminate and this requires taking limits of quotients for evaluation. This difficulty is avoided if we go back to the original differential rate expression and solve it for this particular reactant ratio. Thus, for the second-order reaction with equal initial concentrations of A and B, or for the reaction.



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

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

Plotting the variables as shown in Fig. 3.3 provides a test for this rate expression. In practice we should choose reactant ratios either equal to or widely different from the stoichiometric ratio.

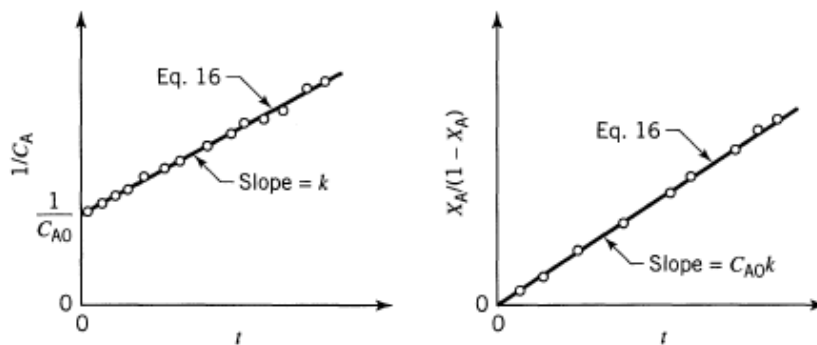


Figure 3.3 Test for the bimolecular mechanisms, $A + B \rightarrow R$ with $C_{A0} = C_{B0}$, or for the second-order reaction of Eq. 15.

Caution 2. The integrated expression depends on the stoichiometry as well as the kinetics. To illustrate, if the reaction:



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

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

When a stoichiometric reactant ratio is used the integrated form is

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

These two cautions apply to all reaction types. Thus, special forms for the integrated expressions appear whenever reactants are used in stoichiometric ratios, or when the reaction is not elementary.

Empirical Rate Equations of nth Order. When the mechanism of reaction is not known, we often attempt to fit the data with an nth-order rate equation of the form

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \quad (20) \quad \longrightarrow \quad C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt, \quad n \neq 1 \quad \dots\dots(21)$$

Select a value for n and calculate k. The value of n which minimizes the variation in k is the desired value of n.

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

$$-r_A = -\frac{dC_A}{dt} = k \quad (22) \quad \longrightarrow \quad \begin{cases} C_{A0} - C_A = C_{A0}X_A = kt & \text{for } t < \frac{C_{A0}}{k} \\ C_A = 0 & \text{for } t \geq \frac{C_{A0}}{k} \end{cases}$$

(23)

Which means that the conversion is proportional to time, as shown in Fig. 3.4. As a rule, reactions are of zero order only in certain concentration ranges-the higher concentrations. If the concentration is lowered far enough, we usually

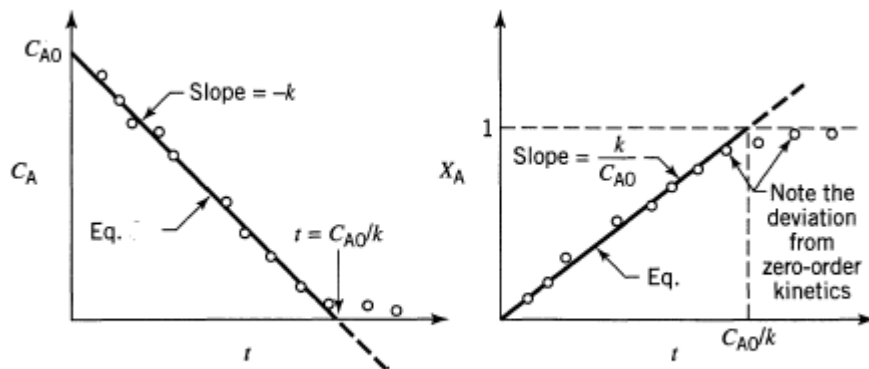


Figure 3.4 Test for a zero-order reaction, or rate equation, Eq. (22).

Find that the reaction becomes concentration-dependent, in which case the order rises from