

# Chapter 2

## Kinetics of Homogeneous Reactions

### Simple Reactor Types

Ideal reactors have three ideal flow or contacting patterns. We show these in Fig. 2.1, and we very often try to make real reactors approach these ideals as closely as possible.

We particularly like these three flow or reacting patterns because they are easy to treat (it is simple to find their performance equations) and because one of them often is the best pattern possible (it will give the most of whatever it is we want). Later we will consider recycle reactors, staged reactors, and other flow pattern combinations, as well as deviations of real reactors from these ideals.

### The Rate Equation

Suppose a single-phase reaction  $aA + bB \rightarrow rR + sS$ . The most useful measure of reaction rate for reactant A is then

$$-r_A = \frac{1}{V} \frac{dN_A}{dt} = \frac{(\text{amount of A disappearing})}{(\text{volume})(\text{time})}, \quad \left[ \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right] \quad (1)$$

rate of disappearance of A

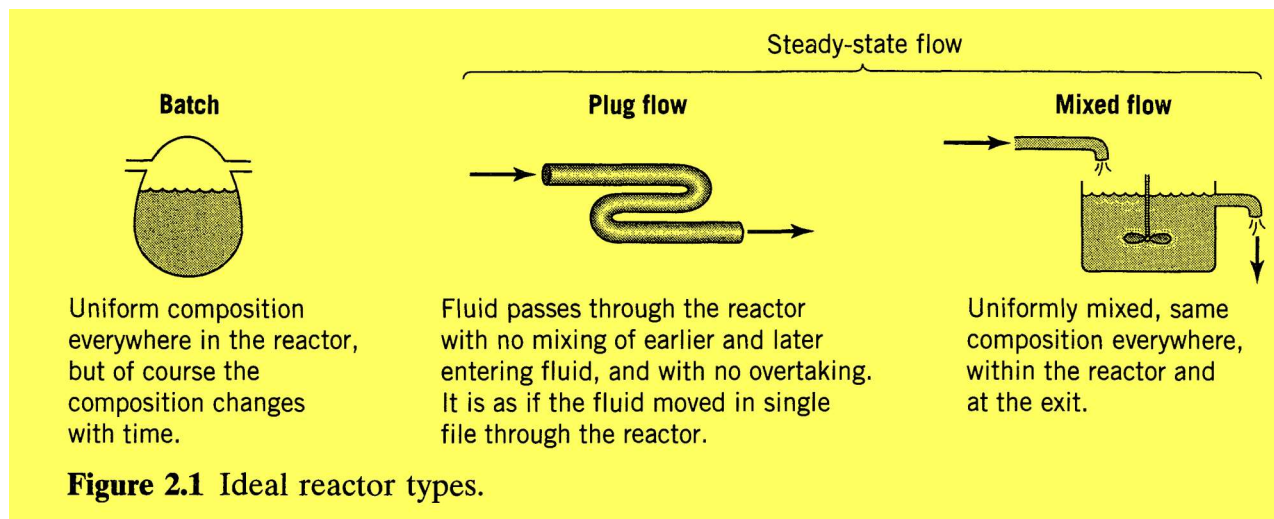
note that this is an intensive measure

the minus sign means disappearance

In addition, the rates of reaction of all materials are related by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

Experience shows that the rate of reaction is influenced by the composition and the energy of the material. By energy we mean the temperature (random kinetic energy of the molecules), the light intensity within the system (this may affect



the bond energy between atoms), the magnetic field intensity, etc. Ordinarily we only need to consider the temperature, so let us focus on this factor. Thus, we can write

$$-r_A = f \left[ \begin{array}{l} \text{temperature} \\ \text{dependent} \\ \text{terms} \end{array} , \begin{array}{l} \text{concentration} \\ \text{dependent} \\ \text{terms} \end{array} \right] \quad \text{as an example} \quad k C_A^a = k_0 e^{-E/RT} C_A^a \quad (2)$$

$\left(\frac{\text{mol}}{\text{m}^3}\right)^{1-a} \text{s}^{-1}$ 
activation energy

reaction order
temperature dependent term

Here are a few words about the concentration-dependent and the temperature-dependent terms of the rate.

## 2.1 CONCENTRATION-DEPENDENT TERM OF A RATE EQUATION

Before we can find the form of the concentration term in a rate expression, we must distinguish between different types of reactions. This distinction is based on the form and number of kinetic equations used to describe the progress of reaction. Also, since we are concerned with the concentration-dependent term of the rate equation, we hold the temperature of the system constant.

### Single and Multiple Reactions

First of all, when materials react to form products it is usually easy to decide after examining the stoichiometry, preferably at more than one temperature, whether we should consider a single reaction or a number of reactions to be occurring.

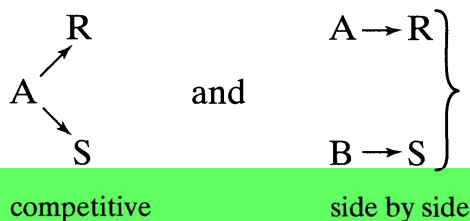
When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, we have a *single reaction*. When more than one stoichiometric equation is chosen to represent the observed changes,

then more than one kinetic expression is needed to follow the changing composition of all the reaction components, and we have *multiple reactions*.

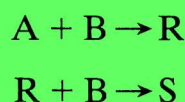
Multiple reactions may be classified as:  
*series reactions*,



*parallel reactions*, which are of two types



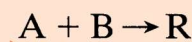
and more complicated schemes, an example of which is



Here, reaction proceeds in parallel with respect to B, but in series with respect to A, R, and S.

## Elementary and Nonelementary Reactions

Consider a single reaction with stoichiometric equation

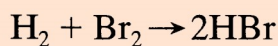


If we postulate that the rate-controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B, then the number of collisions of molecules A with B is proportional to the rate of reaction. But at a given temperature the number of collisions is proportional to the concentration of reactants in the mixture; hence, the rate of disappearance of A is given by

$$-r_A = kC_A C_B$$

Such reactions in which the rate equation corresponds to a stoichiometric equation are called *elementary reactions*.

When there is no direct correspondence between stoichiometry and rate, then we have *nonelementary reactions*. The classical example of a nonelementary reaction is that between hydrogen and bromine,



which has a rate expression\*

$$r_{\text{HBr}} = \frac{k_1[\text{H}_2][\text{Br}_2]^{1/2}}{k_2 + [\text{HBr}]/[\text{Br}_2]} \quad (3)$$

Nonelementary reactions are explained by assuming that what we observe as a single reaction is in reality the overall effect of a sequence of elementary reactions. The reason for observing only a single reaction rather than two or more elementary reactions is that the amount of intermediates formed is negligibly small and, therefore, escapes detection. We take up these explanations later.

## Molecularity and Order of Reaction

The *molecularity* of an elementary reaction is the number of molecules involved in the reaction, and this has been found to have the values of one, two, or occasionally three. Note that the molecularity refers only to an elementary reaction.

Often we find that the rate of progress of a reaction, involving, say, materials A, B, . . . , D, can be approximated by an expression of the following type:

$$-r_A = kC_A^a C_B^b \dots C_D^d, \quad a + b + \dots + d = n \quad (4)$$

where  $a, b, \dots, d$  are not necessarily related to the stoichiometric coefficients. We call the powers to which the concentrations are raised the *order of the reaction*. Thus, the reaction is

$a$ th order with respect to A

$b$ th order with respect to B

$n$ th order overall

Since the order refers to the empirically found rate expression, it can have a fractional value and need not be an integer. However, the molecularity of a reaction must be an integer because it refers to the mechanism of the reaction, and can only apply to an elementary reaction.

For rate expressions not of the form of Eq. 4, such as Eq. 3, it makes no sense to use the term reaction order.

## Rate Constant $k$

When the rate expression for a homogeneous chemical reaction is written in the form of Eq. 4, the dimensions of the rate constant  $k$  for the  $n$ th-order reaction are

$$(\text{time})^{-1}(\text{concentration})^{1-n} \quad (5)$$

\* To eliminate much writing, in this chapter we use square brackets to indicate concentrations. Thus,

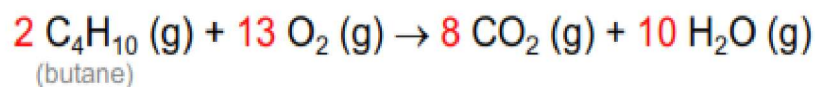
$$C_{\text{HBr}} = [\text{HBr}]$$

which for a first-order reaction becomes simply

$$(\text{time})^{-1} \quad (6)$$

### **EXAMPLE**

When butane is burned it decreases at a rate of 0.20 mol/s.



- What is the rate at which O<sub>2</sub> concentration is decreasing?
- What are the rates at which the product concentrations are increasing?

### **Answers:**

- 0.20 M/s \* 13/2 = 1.3 M/s is the rate that O<sub>2</sub> is consumed.
- 0.20 M/s \* 8/2 = 0.8 M/s is the rate that CO<sub>2</sub> is produced.  
0.20 M/s \* 10/2 = 1.0 M/s is the rate that H<sub>2</sub>O is produced.

## 2.2 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

$$\begin{aligned} r_i &= f_1(\text{temperature}) \cdot f_2(\text{composition}) \\ &= k \cdot f_2(\text{composition}) \end{aligned} \quad (33)$$

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:

$$k = k_0 e^{-E/RT} \quad (34)$$

where  $k_0$  is called the frequency or pre-exponential factor and  $E$  is called the activation energy of the reaction.\* This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency.

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

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (35)$$

provided that  $E$  stays constant.

### Comparison of Theories with Arrhenius' Law

The expression

$$k = k'_0 T^m e^{-E/RT}, \quad 0 \leq m \leq 1 \quad (36)$$

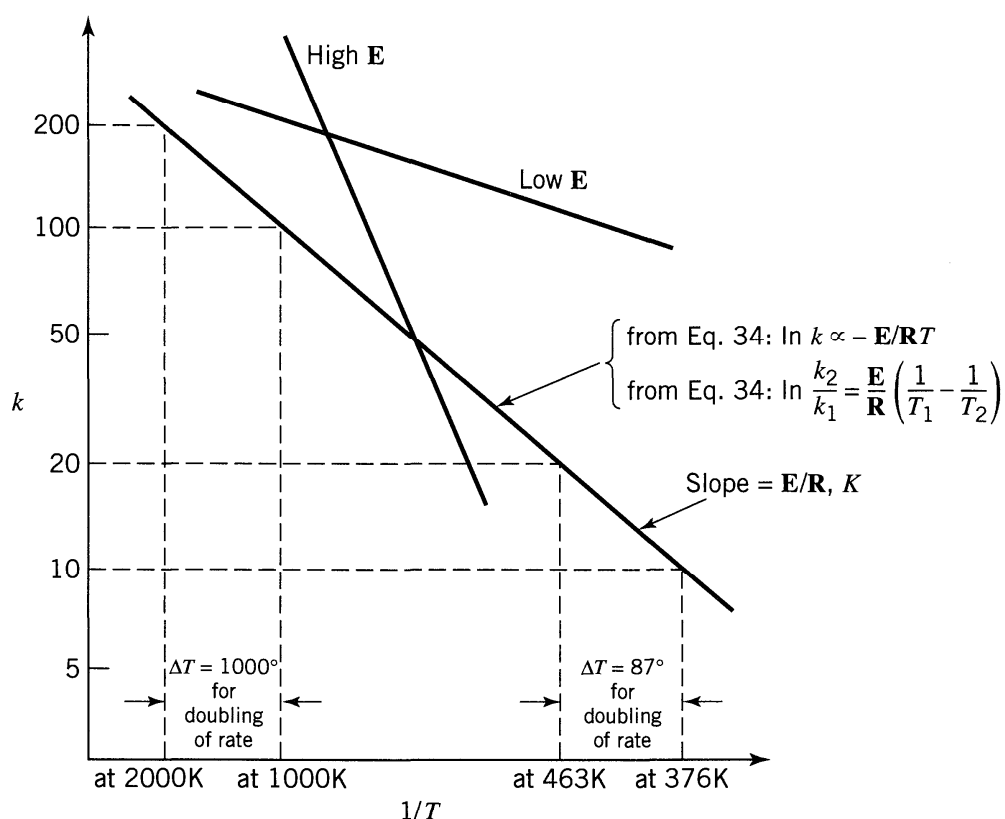
summarizes the predictions of the simpler versions of the collision and transition state theories for the temperature dependency of the rate constant. For more complicated versions  $m$  can be as great as 3 or 4. Now, because the exponential term is so much more temperature-sensitive than the pre-exponential term, the variation of the latter with temperature is effectively masked, and we have in effect

$$k = k_0 e^{-E/RT} \quad (34)$$

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\* There seems to be a disagreement in the dimensions used to report the activation energy; some authors use joules and others use joules per mole. However, joules per mole are clearly indicated in Eq. 34.

But what moles are we referring to in the units of  $E$ ? This is unclear. However, since  $E$  and  $R$  always appear together, and since they both refer to the same number of moles, this bypasses the problem. This whole question can be avoided by using the ratio  $E/R$  throughout.



**Figure 2.2** Sketch showing temperature dependency of the reaction rate.

This shows that Arrhenius' law is a good approximation to the temperature dependency of both collision and transition-state theories.

### Activation Energy and Temperature Dependency

The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction, as illustrated in Fig. 2.2 and Table 2.1. 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.

**Table 2.1** Temperature Rise Needed to Double the Rate of Reaction for Activation Energies and Average Temperatures Shown<sup>a</sup>

Average Temperature	Activation Energy $E$			
	40 kJ/mol	160 kJ/mol	280 kJ/mol	400 kJ/mol
0°C	11°C	2.7°C	1.5°C	1.1°C
400°C	65	16	9.3	6.5
1000°C	233	58	33	23
2000°C	744	185	106	74

<sup>a</sup> Shows temperature sensitivity of reactions.

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 2.3**    **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

$$t_1 = 30 \text{ min} \quad \text{at a} \quad T_1 = 336 \text{ K}$$

$$t_2 = 15 \text{ sec} \quad \text{at a} \quad T_2 = 347 \text{ K}$$

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

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

or

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

from which the activation energy

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