Chapter 35: Elementary Chemical Kinetics

- **Chemical kinetics** involves the study of the rates and mechanisms of chemical reactions,

- Thermodynamic descriptions of chemical reactions involve the Gibbs or Helmholtz energy for a reaction and the corresponding equilibrium constant. These quantities are sufficient to predict the reactant and product concentrations at equilibrium, but are of little use in determining the timescale over which the reaction occurs.

- Thermodynamics may dictate that a reaction is spontaneous, but does it occur in $10^{-15}$ s (a femtosecond) or $10^{15}$ s (the age of the universe)? The answer to this question lies in the domain of chemical kinetics.

  - In the course of a chemical reaction, concentrations will change with time as “reactants” become “products”.

  - The left figure (Fig. 35.1) presents the simple conversion of reactant A into product B. As the reaction proceeds, a decrease in reactant concentration and a corresponding increase in the product concentration is observed.

  - One way to describe this process is to define the rate of concentration change with time, a quantity that is referred to as the reaction rate.
35.1 Introduction to Kinetics

- By monitoring the rate at which chemical reactions occur and determining the dependence of this rate on system parameters such as temperature, concentration and pressure, we can gain insight into the mechanism of reaction.

- Experimental chemical kinetics includes the development of techniques that allow for the study of chemical reactions including the measurement and analysis of chemical reaction dynamics.

- A substantial amount of theoretical work has also been performed to understand reaction mechanisms and the underlying physics that govern the rates of chemical transformations.

- The synergy between experimental and theoretical chemical kinetics has provided for dramatic advances in this field.

- The importance of chemical kinetics is evidenced by its application in nearly every area of chemistry
  - enzyme catalysis
  - materials processing
  - atmospheric chemistry.
35.2 Reaction Rates

- Consider the following “generic” chemical reaction:
  
  \[ aA + bB + \ldots \rightarrow cC + dD + \ldots \]

  In the above Equation, uppercase letters indicate a chemical species and the lowercase letters represent the stoichiometric coefficient for the species in the balanced reaction.

- The species on the left-hand and right-hand sides of the arrow are referred to as **reactants** and **products**, respectively.

- The number of moles of a species during any point of the reaction is given by
  
  \[ n_i = n_i^o + \nu_i \xi \]

  where \( n_i \) is the number of moles of species \( i \) at any given time during the reaction, \( n_i^o \) is the number of moles of species \( i \) present before initiation of the reaction, \( \nu_i \) is related to the stoichiometric coefficient of species \( i \), and \( \xi \) represents the advancement of the reaction and is equal to zero at the start of the reaction.

- The advancement variable allows us to quantify the rate of the reaction with respect to all species, irrespective of stoichiometry. Since reactants will be consumed and products formed during the reaction, \( \nu_i \) is set equal to -1 times the stoichiometric coefficient for reactants, and is set equal to the stoichiometric coefficient for products.
35.2 Reaction Rates

- The time evolution of the reactant and product concentration is quantified by differentiating both sides of the equation representing the number of moles of species with respect to time:
  \[
  \frac{dn_i}{dt} = v_i \frac{d\xi}{dt}
  \]

- The **reaction rate** is defined as the change in the advancement of the reaction with time:
  \[
  \text{Rate} = \frac{d\xi}{dt}
  \]

- With this definition, the rate of reaction with respect to the change in the number of moles of a given species with time is
  \[
  \text{Rate} = \frac{1}{v_i} \frac{dn_i}{dt}
  \]

- As an example of how the rate of reaction is defined relative to the change in moles of reactant or product with time, consider the following reaction:
  \[
  4 \text{ NO}_2 (g) + \text{ O}_2 (g) \rightarrow 2\text{ N}_2\text{O}_5 (g)
  \]

- The reaction rate can be expressed with respect to any species in the above reaction by:
  \[
  \text{Rate} = -\frac{1}{4} \frac{dn_{\text{NO}_2}}{dt} = -\frac{dn_{\text{O}_2}}{dt} = \frac{1}{2} \frac{dn_{\text{N}_2\text{O}_5}}{dt}
  \]

- Notice that the sign convention of the coefficient with respect to reactants and products: negative for reactants and positive for products. Also, note that the rate of reaction can be defined with respect to both reactants and products.
35.2 Reaction Rates

- In the example, 4 moles of NO$_2$ react with 1 mol of O$_2$ to produce 2 mol of N$_2$O$_5$ product. Therefore, the rate of conversion of NO$_2$ will be four times greater than the rate of O$_2$ conversion.

- Although the conversion rates are different, the reaction rate defined with respect to either species will be the same. Furthermore, because both NO$_2$ and O$_2$ are reactants, the change in the moles of these species with respect to time is negative. However, by using a negative stoichiometric coefficient, the reaction rate defined with respect to the reactants is still a positive quantity.

- In applying 4 NO$_2$ (g) + O$_2$ (g) → 2N$_2$O$_5$ (g) to define the rate of reaction, a set of stoichiometric coefficients must be employed; however, these coefficients are not unique. For example, multiplying both sides of the Equation by a factor of 2 the expression for the rate of conversion must also change. Generally, one decides on a given set of coefficients for a balanced reaction and uses these coefficients consistently through a given kinetic problem.

- In the present definition, the rate of reaction as written is an extensive property; therefore, it will depend on the system size. The rate can be made intensive by dividing the Equation by the volume of the system.

\[
R = \frac{Rate}{V} = \frac{1}{V} \left( \frac{1}{v_i} \frac{dn_i}{dt} \right) = \frac{1}{v_i} \frac{d[i]}{dt}
\]

- \(R\) is the intensive reaction rate. The last equality in the Equation is performed recognizing that moles of species \(i\) per unit volume is simply the molarity of species \(i\), or \([i]\). The above Equation is the definition for the rate of reaction at constant volume.
35.2 Reaction Rates

- For species in solution, the application of the Equation in defining the rate of reaction is clear, but it can also be used for gases, as shown in the Example Problem.

- **Example Problem 35.1** The decomposition of acetaldehyde is given by the following balanced reaction:

  \[
  \text{CH}_3\text{COH} \ (g) \rightarrow \text{CH}_4 \ (g) + \text{CO} \ (g).
  \]

  Define the rate of reaction with respect to the pressure of the reactant.

- Focusing on the acetaldehyde reactant, we obtain \( n_{\text{CH}_3\text{COH}} = n^0_{\text{CH}_3\text{COH}} - \xi. \)

- Using the ideal gas law, the pressure of acetaldehyde is expressed as

  \[
  P_{\text{CH}_3\text{COH}} = \frac{n_{\text{CH}_3\text{COH}}}{V} \ RT = [\text{CH}_3\text{COH}]RT
  \]

- Therefore, the pressure is related to the concentration by the quantity \( RT. \) Substituting this result into the Equation for Rate with \( v_i = 1 \) yields

  \[
  R = \frac{\text{Rate}}{V} = -\frac{1}{v_i} \frac{d[\text{CH}_3\text{OH}]}{dt} = -\frac{1}{RT} \frac{dP_{\text{CH}_3\text{OH}}}{dt}
  \]
35.3 Rate Laws

- The rate of a reaction will generally depend on the temperature, pressure, and concentration of species involved in the reaction. In addition, the rate may depend on the phase or phases in which the reaction occurs.

- Homogeneous reactions occur in a single phase, whereas heterogeneous reactions involve more than one phase. Reactions that involve surfaces are classic examples of heterogeneous reactions. We will limit discussion to homogenous reactions (heterogeneous reactions are discussed in Chapter 36).

- For the majority of homogenous reactions, an empirical relationship between reactant concentrations and the rate of chemical reaction can be written. This relationship is known as a rate law, and for the general reaction mentioned previously it is written as \( R = k[A]^\alpha[B]^\beta \ldots \), where \([A]\) is the concentration of reactant A, \([B]\) is the concentration of reactant B, and so forth.

- The constant \( \alpha \) is known as the reaction order with respect to species A, \( \beta \) is the reaction order with respect to species B, and so forth. The overall reaction order is equal to the sum of the individual reaction orders (\( \alpha + \beta + \ldots \)).

- Finally, \( k \) is referred to as the rate constant for the reaction. The rate constant is independent of concentration, but dependent on pressure and temperature, as discussed later.

- The reaction order dictates the concentration dependence of the reaction rate. The reaction order may be integer, zero, or fractional.
35.3 Rate Laws

- The reaction orders have no relation to stoichiometric coefficients, and they are determined by experiments.
- For example, reconsider the reaction of nitrogen dioxide with molecular oxygen:
  \[ 4 \text{NO}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{N}_2\text{O}_5 (g) \]
  The experimentally determined rate law expression for the reaction is
  \[ R = k[\text{NO}_2]^2[\text{O}_2] \]
- That is, the reaction is second order with respect to \( \text{NO}_2 \), first order with respect to \( \text{O}_2 \), and third order overall. Notice that the reaction orders are not equal to the stoichiometric coefficients.
- All rate laws must be determined experimentally with respect to each reactant, and there is no insight to be gained by considering the stoichiometry of the reaction.
- In the rate law expression \( R = k[A]^\alpha[B]^\beta \ldots \), the rate constant serves as the proportionality constant between the concentration of the various species and the reaction rate.
- Inspection of the Equation
  \[ R = \frac{\text{Rate}}{V} = \frac{1}{V} \left( \frac{1}{v_i} \frac{dn_i}{dt} \right) = \frac{1}{v_i} \frac{d[i]}{dt} \]
  demonstrates that the reaction rate will always have units of concentration time\(^{-1}\). Therefore the units of \( k \) must change with respect to the overall order of the reaction to ensure that the reaction rate has correct units. The relationship between the rate law expression, order, and the units of \( k \) is presented in Table 35.1.
35.3.1 Rate Laws – Measuring Reaction Rates

With the definitions for the reaction rate and rate law provided by the earlier equations, the question of how one measures the rate of reaction becomes important.

To illustrate this point, consider the following reaction

\[ \text{A} \rightarrow \text{B} \text{ (with rate constant } k) \]

Furthermore, suppose experiments demonstrate that the reaction is first order in \( \text{A} \), first order overall, and \( k = 40 \text{ s}^{-1} \) so that \( R = k[A] = (40 \text{ s}^{-1})[A] \).

The Equation states that the rate of the reaction is equal to the negative of the time derivative of \([A]\). Imagine that we perform an experiment in which \([A]\) is measured as a function of time as shown in Fig. 35.2.

The derivative of the concentration of \( \text{A} \) is simply the slope of the tangent for the concentration curve at a specific time. Therefore, the reaction rate will depend on the time at which the rate is determined. Fig. 35.2 presents a measurement of the rate at two time points, \( t = 0 \text{ ms} \) and \( t = 30 \text{ ms} \) (\( 1 \text{ ms} = 10^{-3} \text{ s} \)).
35.3.1 Rate Laws – Measuring Reaction Rates

• At \( t = 0 \) ms, the reaction rate is given by the negative of the slope of the line corresponding to the change in \([A]\) with time
  \[
  R_{t=0} = -\frac{d[A]}{dt} = 40 \text{ Ms}^{-1}
  \]

• However, when measured at 30 ms the rate is
  \[
  R_{t=30\text{ms}} = -\frac{d[A]}{dt} = 12 \text{ Ms}^{-1}
  \]

• Notice that the reaction rate is decreasing with time. This behavior is a direct consequence of the change of \([A]\) as a function of time, as expected from the rate law equation. Specifically, at \( t = 0 \),
  \[
  R_{t=0} = 40 \text{ s}^{-1}[A]_{t=0} = 40 \text{ s}^{-1} (1\text{M}) = 40 \text{ Ms}^{-1}
  \]

• However, by \( t = 30 \) ms the concentration of \( A \) has decreased to 0.3 M so that the rate is
  \[
  R_{t=30\text{ms}} = k[A] = (40 \text{ s}^{-1})[A]_{t=30\text{ms}} = 40 \text{ s}^{-1} (0.3 \text{ M}) = 12 \text{ Ms}^{-1}
  \]

• This difference in rates brings to the forefront an important issue in kinetics: how does one define a reaction rate if the rate changes with time?

• One convention is to define the rate before the reaction concentrations have undergone any substantial change from their initial values. The reaction rate obtained under such conditions is known as the initial rate. The initial rate in the previous example is that determined at \( t = 0 \). In the remainder of the chapter, the rate of reaction is taken be synonymous with the initial rate.

• However, the reaction rate constant is independent of concentrations; thus the reaction rate can be determined at any time if the rate constant, concentrations, and order dependence of the reaction rate are known.
35.3.2 Rate Laws – Determining Reaction Orders

- The majority of modern kinetic experiments involve *physical methods*. In these methods a physical property of the system is monitored as the reaction proceeds; example, system pressure or volume.

- More complex physical methods involve techniques that are capable of monitoring the concentration of an individual species as a function of time – spectroscopic techniques such as electronic absorption, vibrational spectroscopy using infrared and Raman, NMR spectroscopy.

- The challenge in chemical kinetics is to perform measurements with sufficient time resolution to monitor the chemistry of interest. In particular, reactions that occur on short timescales (10^{-12} – 10^{-15} s).

- For reactions on timescales as short as 1 ms, *stopped-flow techniques* provide a convenient method by which to measure solution phase reactions. These techniques are exceptionally popular for biochemical studies. A stopped-flow experiment is illustrated in Fig. 35.3. The temporal resolution of the stopped-flow techniques are generally limited by the time it takes for the reactants to mix.

*Figure 35.3*
35.3.2 Rate Laws – Determining Reaction Orders

- Reactions that can be triggered by light are studied using *flash photolysis techniques*. In this technique, the sample is exposed to a temporal pulse of light that initiates the reaction (laser pulses as short as $10^{-15}$ s are available in the visible wavelength).

- Another approach to studying chemical kinetics is that of *perturbation-relaxation methods*. In this approach, a chemical system initially at equilibrium is perturbed such that the system is no longer at equilibrium (e.g., by changing the pressure, pH, or temperature). By following the relaxation of the system back toward equilibrium, the rate constants for the reaction can be determined.

- In summary, the measurement technique chosen for reaction rate determination will depend on both the specifics of the reaction as well as the timescale over which the reaction occurs.
35.4 Reaction Mechanisms

- The order of a reaction with respect to a given reactant is not determined by the stoichiometry of the reaction. The reason for this is that the balanced chemical reaction provides no information with respect to the mechanism of the chemical reaction.

- A reaction mechanism is defined as the collection of individual kinetic processes or elementary steps involved in the transformation of reactants into products.

- The rate law expression for a chemical reaction, including the order of the reaction, is entirely dependent on the reaction mechanism. In contrast, the Gibbs energy for a reaction is dependent on the equilibrium concentration of reactants and products.

- Just as the study of concentrations as a function of reaction conditions provide information on the thermodynamics of the reaction, the study of the reaction rates as a function of reaction conditions provides information on the reaction mechanism.

- All reaction mechanisms consist of a series of elementary reaction steps, or a chemical process that occurs in a single step. The molecularity of a reaction step is the stoichiometric quantity of reactants involved in the reaction step.

- An example of a unimolecular reaction step is the decomposition of a diatomic molecule into its atomic fragments: \( I_2 \rightarrow 2I \) (dissociation rate constant \( k_d \)).
35.4 Reaction Mechanisms

- Although this equation is referred to as a unimolecular reaction, enthalpy changes accompanying the reaction generally involve the transfer of heat through collisions with other neighboring molecules (discussed in detail in Chapter 36).

- Bimolecular reaction steps involve the interaction of two reactants. For example, the reaction of nitric oxide with ozone is a bimolecular reaction:
  \[
  \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(rate constant } k_r)\]

- The importance of elementary reaction steps is that the corresponding rate law expression for the reaction can be written based on the molecularity of the reaction.

- For the unimolecular decomposition of I$_2$, the rate law expression is that of a first-order reaction. For the unimolecular decomposition of I$_2$, the rate law expression for this elementary step is
  \[
  R = -\frac{d[I_2]}{dt} = k_d[I_2]
  \]

- Likewise, the rate law expression for the bimolecular reaction of NO and O$_3$ is
  \[
  R = -\frac{d[NO]}{dt} = k_r[NO][O_3]
  \]

- Comparison of the rate law expressions with their corresponding reactions demonstrates that the order of the reaction is equal to the stoichiometric coefficient. *The equivalence of order and molecularity is only true for elementary reaction steps.*
A common problem in kinetics is identifying which of a variety of proposed reaction mechanisms is the “correct” mechanism. The design of kinetic experiments to differentiate between proposed mechanisms is quite challenging.

Due to the complexity of many reactions, it is often difficult to experimentally differentiate between several potential mechanisms. A general rule of kinetics is that although it may be possible to rule out a proposed mechanism, it is never possible to prove unequivocally that a given mechanism is correct.

The following example illustrates the point. Consider the following reaction:

\[ \text{A} \rightarrow \text{P} \]

As written, the reaction is a simple first-order transformation of reactant A into product P, and it may occur through a single elementary step.

However, the reaction could as well occur through two elementary steps as follows: \( \text{A} \rightarrow \text{I} \) (with rate constant \( k_1 \)) and \( \text{I} \rightarrow \text{P} \) (with rate constant \( k_2 \)). In this mechanism an intermediate species I is formed.

One way to validate the mechanism is to observe the formation of I. However, if the rate of the second step is very fast compared to the rate of the first step, the concentration of \([\text{I}]\) will be quite small and be below the detection limit.

In order for a reaction mechanism to be valid, the order of the reaction predicted by the mechanism must be in agreement with the experimentally determined rate law. In evaluating a reaction mechanism, one must express the mechanism in terms of elementary reaction steps.
## Rate Laws

### TABLE 35.1

Relationship between Rate Law, Order, and the Rate Constant, $k^*$

<table>
<thead>
<tr>
<th>Rate Law</th>
<th>Order</th>
<th>Units of $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate = $k$</td>
<td>Zero</td>
<td>M s$^{-1}$</td>
</tr>
<tr>
<td>Rate = $k[A]$</td>
<td>First order with respect to A</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>First order overall</td>
<td></td>
</tr>
<tr>
<td>Rate = $k[A]^{2}$</td>
<td>Second order with respect to A</td>
<td>M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Second order overall</td>
<td></td>
</tr>
<tr>
<td>Rate = $k[A][B]$</td>
<td>First order with respect to A</td>
<td>M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>First order with respect to B</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Second order overall</td>
<td></td>
</tr>
<tr>
<td>Rate = $k[A][B][C]$</td>
<td>First order with respect to A</td>
<td>M$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>First order with respect to B</td>
<td></td>
</tr>
<tr>
<td></td>
<td>First order with respect to C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Third order overall</td>
<td></td>
</tr>
</tbody>
</table>

*In the units of $k$, M represents mol L$^{-1}$ or moles per liter.*
Integrated rate law expressions provide the predicted temporal evolution in reactant and product concentrations for reactions having an assumed order dependence.

\[ A \rightarrow P \text{ (rate constant } k) \]

\[ R = k[A]^0 \]

\[ R = -\frac{dA}{dt} = k \]

\( k \) is in \([\text{moles/(liter sec)}]\)

Example, Photodecomposition of oxalic acid:
COOH-COOH to form \( \text{H}_2 \) and \( \text{CO}_2 \)

\[ [A] = -kt + [A]_0 \]

\[ t_{1/2} = \frac{[A]_0}{2k} \]
First-Order Reactions

- \( A \rightarrow P \) (rate constant \( k \))

- If the reaction is first order with respect to \([A]\), the corresponding rate law expression is
  \[ R = k[A] \]
  where \( k \) is the rate constant for the reaction.

- The reaction rate can also be written in terms of the time derivative of \([A]\):
  \[ R = -\frac{d[A]}{dt} \]

- Because the reaction rates given by the above Equations are the same, we can write
  \[ \frac{d[A]}{dt} = -k[A] \]

- The differential equation can be integrated as follows:
  \[
  \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -kdtd \Rightarrow \ln\left(\frac{[A]}{[A]_0}\right) = -kt
  \]
  \[ [A] = [A]_0 e^{-kt} \]
First-Order Reactions

- \([A] = [A]_0\) at \(t = 0\)
- If only the reactant is present at \(t = 0\), the sum of reactant and product concentrations at any given time must be equal to \([A]_0\).
- Using this idea, the concentration of product with time for this first-order reaction is:

\[
[P] + [A] = [A]_0 \text{ or } [P] = [A]_0 - [A]
\]

\[
[P] = [A]_0(1 - e^{-kt})
\]

\[
\ln[A] = \ln[A]_0 - kt
\]
Half- Life and First-Order Reactions

- The time it takes for the reactant concentration to decrease to one-half of its initial value is called the half-life of the reaction and is denoted as $t_{1/2}$. For a first-order reaction, substitution of $t_{1/2}$ into the previous Equation results in the following:

\[-kt_{1/2} = \ln\left(\frac{[A]_0/2}{[A]_0}\right) = -\ln 2 \quad t_{1/2} = \frac{\ln 2}{k}\]

- $t_{3/4} = (2\ln2)/k \Rightarrow t_{3/4} / t_{1/2} = 2$  \quad (t_{3/4} \text{ when } [A] = \frac{1}{4} [A]_0)

- **Example Problem 35.3.** The decomposition of N$_2$O$_5$ is an important process in tropospheric chemistry. The half life for the first-order decomposition of this compound is 2.05 x 10$^4$ s. How long will it take for a sample of N$_2$O$_5$ to decay to 60% of its initial value?

- Radioactive decay of unstable nuclear isotopes is an important example of a first-order process. The decay rate is usually stated as the half-life.

- **Example Problem 35.4** Carbon-14 is a radioactive nucleus with a half-life of 5760 years. Living matter exchanges carbon with its surroundings so that a constant level of $^{14}$C is maintained, corresponding to 15.3 decay events per minute. Once living matter has died, carbon contained in the matter is not exchanged with the surroundings, and the amount of $^{14}$C that remains in the dead material decreases with time due to radioactive decay. Consider a piece of fossilized wood that demonstrates 2.4 $^{14}$C decay events per minute. How old is the wood?
The ratio of decay events yields the amount of $^{14}$C currently present versus the amount that was present when the tree died:

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} = 2.40 \text{ min}^{-1}/15.3 \text{ min}^{-1} = 0.157$$

The rate constant for isotope decay is related to the half-life as follows:

$$k = \ln 2/t_{1/2} = \ln 2/5760 \text{ years} = \ln 2/1.82 \times 10^{11} \text{ s} = 3.81 \times 10^{-12} \text{ s}^{-1}$$

With the rate constant and ratio of isotope concentrations, the age of the fossilized wood is readily determined:

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} = e^{-kt}$$

$$\ln\left(\frac{[^{14}\text{C}]}{[^{14}\text{C}]_0}\right) = -kt$$

$$-1/k \ln\left(\frac{[^{14}\text{C}]}{[^{14}\text{C}]_0}\right) = -1/3.81 \times 10^{-12} \text{ s} \ln(0.157) = t$$

$$4.86 \times 10^{11} \text{ s} = t$$

This time corresponds to an age of approximately 15,400 years


Second-Order Reactions (Type I)

- Consider the following reaction, which is second order with respect to the reactant A: \(2A \rightarrow P\) (with rate constant \(k\)).

- **Second-order reactions** involving a single reactant species are referred to as type \(I\).

- We focus on the type \(I\) case. For this reaction, the corresponding rate law expression is \(R = k[A]^2\).

- The rate is expressed as the derivative of the reactant concentration is

\[
R = -\frac{1}{2} \frac{dA}{dt}
\]

Because of the equivalence with the earlier Equation

\[
- \frac{d[A]}{dt} = 2k[A]^2
\]

- Generally, the quantity \(2k\) is written as an effective rate constant, denoted as \(k_{eff}\).
For a second-order reaction, a plot of the inverse of reactant concentration versus time will result in a straight line having a slope of $k_{\text{eff}}$ and $y$ intercept of $1/[A]_0$.

Second-Order Reactions (Type I)

\[
-t \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_0^t k_{\text{eff}} \, dt
\]

\[
\frac{1}{[A]} - \frac{1}{[A]_0} = k_{\text{eff}} t
\]

\[
\frac{1}{[A]} = \frac{1}{[A]_0} + k_{\text{eff}} t
\]
Half-life is when the concentration of a reactant is half of its initial value.

With this definition, the half-life for a type I second-order reaction is

\[ t_{1/2} = \frac{1}{k_{\text{eff}} [A]_0} \]

In contrast to first order reactions, the half-life for a second-order reaction is dependent on the initial concentration of reactant, with an increase in initial concentration resulting in a decrease in \( t_{1/2} \).

First-order reaction occurs through a unimolecular process, whereas the second-order reaction involves a bimolecular process in which the concentration dependence of the reaction rate is anticipated.

\[ t_{3/4} = \frac{(3)}{k_{\text{eff}} [A]_0} \Rightarrow t_{3/4} / t_{1/2} = 3 \]
Second Order Reactions (Type II)

- Second-order reactions of type II involves two different reactants, \( A \) and \( B \), as follows: \( A + B \to P \) (rate constant \( k \)).

- Assuming that the reaction is first order in both \( A \) and \( B \), the reaction rate is
  \[
  R = k [A][B]
  \]

- In addition, the rate with respect to the time derivative of the reactant concentrations is
  \[
  R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}
  \]

- Note that the loss rate for the reactants is equal such that
  \[
  [A]_0 - [A] = [B]_0 - [B] \\
  [B]_0 - [A]_0 + [A] = [B] \\
  \Delta + [A] = [B]
  \]

- The above Equation provides a definition for \( [B] \) in terms of \( [A] \) and the difference in initial concentration, \( [B]_0 - [A]_0 \), denoted as \( \Delta \).

- With this definition, the integrated rate law expression can be solved as follows:
  \[
  \frac{d[A]}{dt} = -k[A][B] = -k[A](\Delta + [A]) \Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A](\Delta + [A])} = -\int_0^t k \, dt
  \]
Second Order Reactions (Type II)

- Solution to the integral involving \([A]\) is given by
  \[
  \int \frac{dx}{x(c + x)} = -\frac{1}{c} \ln\left(\frac{c + x}{x}\right)
  \]

- Using this solution to the integral, the integrated rate law expression becomes
  \[
  -\frac{1}{\Delta} \ln\left(\frac{\Delta + [A]}{[A]_0}\right) = -kt \Rightarrow \frac{1}{\Delta} \left[ \ln\left(\frac{\Delta + [A]}{[A]_0}\right) - \ln\left(\frac{\Delta + [A]}{[A]_0}\right) \right] = kt
  \]

- The above Equation is not applicable in the case for which the initial concentration are equivalent, that is, when \([B]_0 = [A]_0\).

- For this specific case, the concentration of \([A]\) and \([B]\) reduce to the expression for a second-order reaction of type I with \(k_{\text{eff}} = k\).

- The time evolution in reactant concentrations depends on the amount of each reactant present.

- The concept of half-life does not apply to second-order reactions of type II. Unless the reactants are mixed in stoichiometric proportions (1:1 for the case discussed in this section), the concentration of both species will not be \(\frac{1}{2}\) their initial concentrations at the identical time.
Rate Laws – Determining Reaction Orders

• A + B → C (rate constant k).
  The rate expression for this reaction is: \( R = k[A]^\alpha[B]^\beta \)

• **Isolation (Flooding) method:** the reaction is performed with all the species but one in excess

• Take \([B]_o \ll [A]_o\) e.g. flood system with A. Then \([A] \sim [A]_o\)

• So that \( -d[B]/dt = k'[B]^\beta \), where \( k' = k[A]_o^\alpha \)

• The reaction then becomes pseudo \( \beta \)-order with one reactant

• In the reaction A + B → C, the experiment can be performed where the initial concentration of A is 1.00 M (excess) and the concentration of B is 0.01 M. The rate of reaction will be zero when all the reactant B has been used; however, the concentration of A will have reduced to 0.99, only a slight reduction from the initial concentration

• Since A is in excess, the rate equation simplifies to \( R = k'[B]^\beta \), where \( k' \) is the product of the original rate constant and \([A]^\alpha\), both of which are time independent

• A similar approach can be used to determine \( \alpha \) by performing measurements with B in excess
Method of initial rates: the concentration of a single reactant is changed while holding all other concentrations constant, and the initial rate of reaction determined.

Consider again the reaction: \( A + B \rightarrow C \). To determine the order of the reaction, the reaction rate is measured as \([A]\) is varied and the concentration of \(B\) is held constant.

The reaction rate at two different values of \([A]\) is then analyzed to determine the order of the reaction with respect to \([A]\):

\[
\frac{R_1}{R_2} = \frac{k[A]^\alpha [B]^\beta}{k[A]^\alpha_0 [B]^\beta_0} = \left(\frac{[A]_1}{[A]_2}\right)^\alpha \quad \text{or} \quad \ln\left(\frac{R_1}{R_2}\right) = \alpha \ln\left(\frac{[A]_1}{[A]_2}\right)
\]

- If \(2[A]_2 = [A]_1\) then, if \(R_1/R_2 = 1\) then \(\alpha = 0\)
  - \(R_1/R_2 = 2\) then \(\alpha = 1\)
  - \(R_1/R_2 = 4\) then \(\alpha = 2\)

A similar approach where \([A]\) is held constant can be used to determine \(\beta\).

Example Problem 35.2 illustrates the determination of the order of the reaction and rate constants using the method of initial rates.
Numerical Approaches

- There is a wide variety of kinetic problems for which an integrated rate law expression cannot be obtained. How can one compare a kinetic model with experiment in the absence of an integrated rate law?

- In such cases, numerical methods provide another approach by which to determine the time evolution in concentrations predicted by a kinetic model.

- To illustrate this approach, consider the following first-order reaction:
  \[ A \rightarrow P \text{ (rate constant } k) \]

The differential rate expression for this reaction is

\[ \frac{d[A]}{dt} = -k[A] \]

- The time derivative corresponds to the change in [A] for a time duration that is infinitesimally small. Using this idea we can state that for a finite time duration, \( \Delta t \), the change in [A] is given by

\[ \frac{\Delta[A]}{\Delta t} = -k[A] \text{ or } \Delta[A] = -\Delta t(k[A]) \]

- In the above Equation, [A] is the concentration of A at a specific time. Therefore, we can use this equation to determine the change in the concentration of A, or \( \Delta[A] \), over a time period \( \Delta t \) and then use this concentration change to determine the concentration at the end of the time period.

- This new concentration can be used to determine the subsequent change in [A] over the next time period, and this process is continued until the reaction is complete.
• Mathematically, 
\[ [A]_{t + \Delta t} = [A]_t + \Delta[A] = [A]_t + \Delta t(-k[A]_t) = [A]_t - k \Delta t[A]_t \]

• In the above Equation, \([A]_t\) is the concentration at the beginning of the time interval, and \([A]_{t+\Delta t}\) is the concentration at the end of the interval. The process is illustrated in Figure 35.6 over a number of time intervals.

• The example discussed here is representative of the general approach to numerically integrating differential equations, known as Euler's method. Application of Euler's method requires some knowledge of the timescale of interest, and then selection of a time interval, \(\Delta t\), that is sufficiently small to capture the evolution in concentration.

• Figure 35.7 presents a comparison of the reactant concentration determined using the integrated rate law expression for a first-order reaction to that determined numerically for three different choices for \(\Delta t\).

• The method is “brute force” in that a sufficiently small step must be chosen to accurately capture the slope of the concentration, and the time steps must be sufficiently small.
Sequential (Series) First-Order Reactions

- Consider the following *sequential (series) reaction* scheme:

  \[ A \xrightarrow{k_A} I \xrightarrow{k_I} P \]

- In this scheme, the reactant A decays to form intermediate I, and this intermediate undergoes subsequent decay resulting in the formation of product P.

- The sequential reaction scheme involves a series of elementary first-order reactions

  \[
  \frac{d[A]}{dt} = -k_A[A]; \quad \frac{d[I]}{dt} = k_A[A] - k_I[I]; \quad \text{and} \quad \frac{d[P]}{dt} = k_I[I]
  \]

- How do we determine the concentration of each species as a function of time?

- Let only the reactant A be present at \( t = 0 \) such that \([A]_0 \neq 0; [I]_0 = 0; [P]_0 = 0.\) With these initial conditions, the expression for \([A]\) is exactly that derived previously:

  \[ [A] = [A]_0 e^{-k_At} \]
Sequential First-Order Reactions

- The expression for \([A]\) can be substituted into the differential rate expression for \(I\) resulting in
  \[
  \frac{d[I]}{dt} = k_A[A] - k_I[I] = k_A[A]_0 e^{-k_A t} - k_I[I]
  \]

- \[
  \frac{d[I]}{dt} + k_I = k_A[A]_0 e^{-k_A t}
  \]

- Multiply by \(e^{k_I t}\) on both sides
  \[
  e^{k_I t} \left[ \frac{d[I]}{dt} + k_I[I] \right] = k_A[A]_0 e^{(k_I - k_A) t} \quad \Rightarrow \quad \frac{d}{dt} [I e^{k_I t}] = k_A[A]_0 e^{(k_I - k_A) t}
  \]

- \[
  \int d[I] e^{k_I t} = \int k_A[A]_0 e^{(k_I - k_A) t} dt
  \]

- Integrate between \(I_0\) to \(I\) (lhs) and \(0\) to \(t\) (rhs)

- The equation when solved yield the following expression for \([I]\):
  \[
  [I] = \frac{k_A}{k_I - k_A} (e^{-k_A t} - e^{-k_I t})[A]_0
  \]
Sequential First-Order Reactions

Finally, the expression for \([P]\) is readily determined using the initial conditions of the reactions, with the initial concentration of \(A\), \([A]_0\), equal to the sum of all concentrations for \(t > 0\):

\[
[A]_0 = [A] + [I] + [P] \\
[P] = [A]_0 - [A] - [I]
\]

Substitution of expressions for \([A]\) and \([I]\) results in the following expression for \([P]\):

\[
[P] = \left( \frac{k_Ae^{-k_At} - k_Ie^{-k_At}}{k_I - k_A} + 1 \right) [A]_0
\]
Sequential First-Order Reactions

- (a) Evolution in concentration when $k_A = 2k_I$
  - ‘$A$’ undergoes exponential decay resulting in the production of $I$.
  - intermediate in turn undergoes subsequent decay to form the product.
  - temporal evolution of $[I]$ is extremely dependent on the relative rate constants for the production, $k_A$, and decay, $k_I$.

- (b) Evolution in concentration when $k_A >> k_I$
  - maximum intermediate concentration is greater than in the first case.

- (c) Evolution in concentration when $k_A < k_I$
  - maximum in intermediate concentration is significantly reduced
  - if intermediate undergoes decay at a faster rate than the rate at which it is formed, then the intermediate concentration will be small. Opposite logic holds as evidenced by $k_A >> k_I$ example presented in (b)
The maximum intermediate concentration is reached when the derivative of \([I]\) with respect to time is equal to zero:

\[
\left( \frac{d[I]}{dt} \right)_{t = t_{\text{max}}} = 0
\]

Using the expression for \([I]\) in the previous slide, the time at which \([I]\) is at a maximum, \(t_{\text{max}}\), is

\[
t_{\text{max}} = \frac{1}{k_A - k_I} \ln \left( \frac{k_A}{k_I} \right)
\]

Example Problem 35.5 Determine the time at which \([I]\) is at a maximum for \(k_A = 2k_I = 0.1 \text{ s}^{-1}\).

Derive expressions for \([A]\), \([I]\) and \([P]\) when \(k_A = k_I\). Then determine \(t_{\text{max}}\).
Rate-Determining Steps

- The rate of product formation in a sequential reaction depends on the timescale for production and decay of the unimolecular species

Limiting Conditions:

- Rate constant for intermediate decay is much greater than the rate constant for production, \( k_i > k_A \)
  - any intermediate formed will rapidly go on to product, and the rate of product formation depends on the rate of reactant decay

- Rate constant for intermediate production is significantly greater than the intermediate decay rate, \( k_A > k_i \)
  - reactants quickly produce intermediate, but the rate of product formation depends on the rate of intermediate decay

- Important approximation made in the analysis of kinetic problems, that of the rate-determining step or the rate limiting step

- If one step in the sequential reaction is much slower than any other step, this slow step will control the rate of product formation and is therefore the rate-determining step
Rate-Determining Steps

- Consider the sequential reaction considered previously when \( k_A >> k_I \)

\[
A \xrightarrow{k_A} I \xrightarrow{k_I} P
\]

- In this limit, the kinetic step corresponding to the decay of intermediate \( k_I \) is the rate-limiting step

- Because \( k_A >> k_I \), \( e^{-k_A t} << e^{-k_I t} \), and the expression for \([P]\) becomes

\[
\lim [P] = \lim \left( \left( \frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right) [A]_0 \right) \quad \text{for} \quad k_A \to \infty = (1 - e^{-k_I t}) [A]_0
\]

- The time dependence of \([P]\) when \( k_I \) is the rate-limiting step is identical to that predicted for first-order decay of I resulting in product formation

- The other limit occurs when \( k_I >> k_A \), where \( e^{-k_I t} << e^{-k_A t} \), and the expression for \([P]\) becomes:

\[
\lim [P] = \lim \left( \left( \frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right) [A]_0 \right) \quad \text{for} \quad k_I \to \infty = (1 - e^{-k_A t}) [A]_0
\]

- In this limit, the time dependence of \([P]\) is identical to that predicted for the first-order decay of the reactant A, resulting in product formation

- The rate-determining step approximation is appropriate for the two-step-reaction under consideration with 20-fold differences between the rate constants.
**Rate-Determining Steps**

- Comparison of [P] determined using the exact result and the rate-limited prediction, for the cases where \( k_A = 20 \) \( k_f = 1 \) s\(^{-1}\) and where \( k_A = 0.04 \) \( k_f = 0.02 \) s\(^{-1}\).

- In (a), decay of the intermediate is the rate-limiting step in product formation. Rapid reactant decay, resulting in an appreciable intermediate concentration, with the subsequent decay of the intermediate reflected by a corresponding increase in [P].

- The similarity of the exact and rate-limiting curves for [P] demonstrates the validity of the rate-limiting approximation for this ratio of rate constants.

- The opposite limit is presented in (b). In this case, decay of the reactant is the rate-limiting step in product formation.

- When reactant decay is the rate-limiting step, very little intermediate is produced. In this case, the loss of [A] is mirrored by an increase in [P].

- The agreement between the exact and rate-limiting descriptions of [P] demonstrates the validity of the rate-limiting approximation when a substantial difference in rate constants for intermediate production and decay exists.
The Steady-State Approximation

- Consider the following reaction scheme:

\[
A \xrightarrow{k_A} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} P
\]

- In this reaction, product formation results from the formation and decay of two intermediate species, \( I_1 \) and \( I_2 \). The differential rate expression for this scheme are as follows:

\[
\frac{d[A]}{dt} = -k_A[A]; \quad \frac{d[I_1]}{dt} = k_A[A] - k_1[I_1]; \quad \frac{d[I_2]}{dt} = k_1[I_1] - k_2[I_2]; \quad \text{and} \quad \frac{d[P]}{dt} = k_2[I_2]
\]

- A determination of the time-dependent concentrations for the species involved in this reaction by integration of the differential rate expression is not trivial.

- One approach is to determine numerically the concentrations as a function of time. The results of this approach for \( k_A = 0.02 \text{ s}^{-1} \) and \( k_1 = k_2 = 0.2 \text{ s}^{-1} \) is presented in the figure.

- The figure illustrates that in addition to the modest intermediate concentrations, \( I_1 \) and \( I_2 \) change very little with time such that the time derivative of these concentrations can be set approximately equal to zero:

\[
\frac{d[I]}{dt} = 0
\]
The Steady-State Approximation

• This is known as the **steady-state approximation.**

• This approximation is particularly good when the decay rate of the intermediate is greater than the rate of production so that the intermediates are present at very small concentrations during the reaction (as in the case illustrated in the figure).

• Applying the steady-state approximation to $I_1$ results in the following expression for $[I_1]$:
  $$\frac{d[I_1]_{ss}}{dt} = 0 = k_A[A] - k_1[I_1]_{ss} \Rightarrow [I_1]_{ss} = \frac{k_A}{k_1} [A] = \frac{k_A}{k_1} [A]_0 e^{-k_A t}$$

• The corresponding expression for $[I_2]$ under the steady-state approximation is
  $$\frac{d[I_2]_{ss}}{dt} = 0 = k_1[I_1] - k_2[I_2]_{ss} \Rightarrow [I_2]_{ss} = \frac{k_1}{k_2} [I_1]_{ss} = \frac{k_A}{k_2} [A]_0 e^{-k_A t}$$

• Finally, the differential expression for $P$ is:
  $$\frac{d[P]_{ss}}{dt} = k_2 [I_2] = k_A [A]_0 e^{-k_A t}$$

• Integration results in the familiar expression for $[P]$:
  $$[P]_{ss} = [A]_0 (1 - e^{-k_A t})$$

• Within the steady-state approximation, $[P]$ is predicted to demonstrate appearance kinetics consistent with the first-order decay of $A$. 
The Steady-State Approximation

- When is the steady-state approximation valid?
- The approximation requires that the concentration of intermediate be constant as a function of time.
- Consider the concentration of the first intermediate under the steady-state approximation. The time derivative of \([I_1]_{ss}\) is

\[
\frac{d[I_1]_{ss}}{dt} = \frac{d}{dt} \left( \frac{k_A}{k_1} [A]_0 e^{-k_1 t} \right) = -\frac{k_2^2}{k_1} [A]_0 e^{-k_1 t}
\]

- The steady-state approximation is valid when the above equation is equal to zero, which is true when \(k_1 >> k_A^2 [A]_0\). In other word, \(k_1\) must be sufficiently large that \([I_1]\) is small at all times. Similar logic applies to \(I_2\) for which the steady-state approximation is valid if \(k_2 >> k_A^2 [A]_0\).
- The figure presents a comparison between numerically determined concentrations and those determined using the steady-state approximation. Notice that even for the chosen conditions where the steady-state approximation is expected to be valid, the discrepancy between \([P]\) determined by numerical evaluation versus the steady-state approximation, \([P]_{ss}\) is evident.
- Example Problem 35.6. Single intermediate in seq. rxn.

\[
k_A = 0.02 \text{ s}^{-1}
\]
\[
k_1 = k_2 = 0.2 \text{ s}^{-1}
\]
Parallel Reactions

- In many instances a single reactant can become a variety of products. Such reactions are referred to as **parallel reactions**.

- Consider the following reaction in which the reactant A can form one of two products, B or C:

\[
B \xrightleftharpoons[k_B]{k_C} A \xrightarrow{k_C} C
\]

- The differential rate expression for the reactant and products are:

\[
\frac{d[A]}{dt} = -k_B[A] - k_C[A] = -(k_B + k_C)[A]
\]

\[
\frac{d[B]}{dt} = k_B[A]
\] and \[
\frac{d[C]}{dt} = k_C[A]
\]

- Integration of the preceding expressions involving [A] with the initial condition [A]_0 \neq 0 and [B] = [C] = 0 yields

\[
[A] = [A]_0 e^{-(k_B + k_C)t}
\]

- The product concentrations can be determined by substituting the expression for [A] into the differential expressions and integrating, which results in

\[
[B] = \frac{k_B}{k_B + k_C}[A]_0 \left(1 - e^{-(k_B + k_C)t}\right)
\]

\[
[C] = \frac{k_C}{k_B + k_C}[A]_0 \left(1 - e^{-(k_B + k_C)t}\right)
\]
Parallel Reactions

- The figure provides an illustration of the reactant and product concentrations for this branching reaction where $k_B = 2k_C = 0.1 \text{ s}^{-1}$.
- Notice that the decay of A occurs with an apparent rate constant equal to $k_B + k_C$, the sum of the rate constants for each reaction branch.
- In addition, the ratio of product concentrations is independent of time. This is consistent with the previous equations from which the product concentrations is predicted to be

$$\frac{[B]}{[C]} = \frac{k_B}{k_C}$$

- The equation states that as the rate constant for one of the reaction branches increases relative to the other, the greater the final concentration of the corresponding product will be.
- Furthermore, there is no time dependence in the equation; therefore, the product ratio remains constant with time.
- The results demonstrate that the extent of product formation in a parallel reaction is dependent on the rate constants.
Parallel Reactions

- The yield, $\Phi$, is defined as the probability that a given product will be formed by decay of the reactant:

$$\Phi_i = \frac{k_i}{\sum_n k_n}$$

- In the above equation, $k_i$ is the rate constant for the reaction leading to formation of the product of interest indicated by the subscript $i$. The denominator is the sum over all rate constants for the reaction branches $\sum_i \Phi_i = 1$

- In the example reaction depicted in figure (previous slide) where $k_B = 2k_C$, the yield for the formation of product C is

$$\Phi_C = \frac{k_C}{k_B + k_C} = \frac{k_C}{(2k_C) + k_C} = \frac{1}{3}$$

- Because there are only two branches in this reaction, $\Phi_B = 2/3$. Inspection of figure reveals that $[B] = 2[C]$, which is consistent with the calculated yields

- Example Problem 35.7. In acidic conditions, benzyl penicillin (BP) undergoes parallel reactions to produce three products (rate constants given). Calculate the yield of a one product $P_1$. 


Parallel 1st and 2nd Order Reactions

\[ A \xrightarrow{k_1} B \quad \text{First order reaction} \]

\[ A \xrightarrow{k_2} C \quad \text{Second order reaction} \]

\[- \frac{d[A]}{dt} = k_1[A] + k_2[A]^2; \quad \frac{d[B]}{dt} = k_1[A]; \quad \text{and} \quad \frac{d[C]}{dt} = k_2[A]^2\]

Use the integral solution

\[ \int \frac{dx}{x(ax + b)} = \frac{1}{b} \ln\left(\frac{x}{ax + b}\right) \]

\[ \Rightarrow [A] = \frac{k_1[A]_0}{e^{k_1t}(k_1 + k_2[A]_0) - k_2[A]_0} \]

**Limiting cases:**

For \( k_2[A]_0 \ll k_1 \quad [A] = [A]_0 e^{-k_1t} \quad \text{Apparent First Order reaction} \)

For \( k_2[A]_0 \gg k_1 \) with small values of \( k_1t \quad \text{Apparent Second Order reaction} \)

(Write formula in the form of second order and then use Taylor expansion approx.)
Temperature Dependence of Rate Constants

- Rate constants $k$ are generally temperature dependent quantities.
- Experimentally, it is observed that for many reactions a plot of $\ln (k)$ versus $T^{-1}$ demonstrates linear to close to linear behavior.
- The following empirical relationship between temperature and $k$, first proposed by Arrhenius in the late 1800s, is known as the Arrhenius expression:
  \[ k = Ae^{-E_a / RT} \]
- In the above equation, the constant $A$ is referred to as the frequency factor or Arrhenius preexponential factor, and $E_a$ is the activation energy for the reaction.
- The units of the preexponential factor are identical to those of the rate constant and will vary depending on the order of the reaction. The activation energy is in units of energy mol$^{-1}$ (for example, kJ mol$^{-1}$).
- The natural log of the above equation results in the following expression:
  \[ \ln(k) = \ln(A) - \frac{E_a}{R} \frac{1}{T} \]
- This equation predicts that a plot of $\ln(k)$ versus $T^{-1}$ will yield a straight line with slope equal to $-E_a/R$ and $y$ intercept equal to $\ln(A)$.
- Example Problem 35.8 provides an example of the application of the equation to determine the Arrhenius parameter for a reaction.
• The origin of the energy term in the Arrhenius expression can be understood as follows
  - The activation energy corresponds to the energy needed for the chemical reaction to occur
  - Conceptually, a chemical reaction can be envisioned as occurring along an energy profile as illustrated in figure
  - If the reactants have an energy greater than the activation energy, the reaction can proceed
  - The exponential dependence on the activation energy is consistent with Boltzmann statistics, with \( \exp(-E_a/RT) \) representing the fraction of molecules with sufficient energy to undergo reaction
  - As the activation energy increases, the fraction of molecules with sufficient energy to react will decrease as will the reaction rate.
Temperature Dependence of Rate Constants

- Not all chemical reactions demonstrate Arrhenius behavior.
- The inherent assumption in the Equation $\ln(k) = \ln(A) - \frac{E_a}{R} \frac{1}{T}$ is that both $E_a$ and $A$ are temperature-independent quantities.
- However, there are many reactions for which a plot of $\ln(k)$ versus $T^{-1}$ does not yield a straight line, consistent with the temperature dependence of one or both of the Arrhenius parameters.
- Modern theories of reaction rates predict that the rate constant will demonstrate the following behavior:
  \[ k = a T^m e^{-E'/RT} \]
  where $a$ and $E'$ are temperature-independent quantities, and $m$ can assume values such as 1, $\frac{1}{2}$, and $-\frac{1}{2}$ depending on the details of the theory used to predict the rate constant.
- Although the limitations of the Arrhenius expression are well known it still provides an adequate description of the temperature dependence of reaction rate constants for a wide variety of materials.
In 1896 the Swedish scientist Svante Arrhenius published a new idea. By burning fossil fuels such as coal, thus adding CO₂ to Earth's atmosphere, humanity would raise the planet's average temperature. This "greenhouse effect," as it later came to be called, was only one of many speculations about climate change, and not the most plausible. The few scientists who paid attention to Arrhenius used clumsy experiments and rough approximations to argue that our emissions could not change the planet. Most people thought it was already obvious that puny humanity could never affect the vast global climate cycles, which were governed by a benign "balance of nature."

http://history.aip.org/climate/co2.htm