

■ Kinetics and Arrhenius Equation

1. Kinetics

Zero Order Reaction

A reaction is of zero order when the rate of reaction is independent of the concentration of materials. The rate of reaction is a constant. When the limiting reactant is completely consumed, the reaction stops abruptly.

The zero order rate law for the general reaction



is written as the equation

$$-\frac{d[A]}{dt} = k \quad (1)$$

which on integration of both sides gives

$$[A] = -kt + C \quad (2)$$

When $t = 0$ the concentration of A is $[A]_0$. The constant of integration must be $[A]_0$.

Now the integrated form of zero-order kinetics can be written as follows

$$[A] = -kt + [A]_0 \quad (3)$$

Plotting $[A]$ versus t will give a straight line with slope $-k$.

First Order Reaction

A general unimolecular reaction



where A is a reactant and P is a product is called a first-order reaction.

The rate is proportional to the concentration of a single reactant raised to the first power.

The decrease in the concentration of A over time can be written as:

$$v = -\frac{d[A]}{dt} = k[A] \quad (1)$$

$$-\frac{d[A]}{[A]} = k dt \quad (2)$$

Equation (2) represents the differential form of the rate law. Integration of this equation and determination of the integration constant C produces the corresponding integrated law.

Integrating equation (2) yields:

$$\ln[A] = -kt + C \quad (3)$$

The constant of integration C can be evaluated by using boundary conditions. When $t = 0$, $[A] = [A]_0$. $[A]_0$ is the original concentration of A.

Substituting into equation (3) gives:

$$\ln[A]_0 = -k(0) + C \quad (4)$$

Therefore the value of the constant of integration is:

$$C = \ln[A]_0 \quad (5)$$

Substituting (5) into (4) leads to:

$$\ln \frac{[A]}{[A]_0} = -kt \quad (6)$$

Plotting $\ln[A]$ or $\ln[A]/[A]_0$ against time creates a straight line with slope $-k$. The plot should be linear up to a conversion of 80-90%, that is up to the point at which 80-90% of the concentration of the reactant is consumed.

Equation (6) can also be written as:

$$[A] = [A]_0 e^{-kt} \quad (7)$$

This means that the concentration of A decreases exponentially as a function of time.

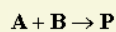
The rate constant k can also be determined from the half-life $t_{1/2}$. Half-life is the time it takes for the concentration to fall from $[A]_0$ to $[A]_0/2$.

According to equation (6) is obtained:

$$k t_{1/2} = \ln \frac{[A]_0}{[A]_0/2} \quad \text{or} \quad k = \frac{\ln 2}{t_{1/2}} \quad (8)$$

Pseudo First Order Reaction

A and B react to produce P:



If the initial concentration of the reactant A is much larger than the concentration of B, the concentration of A will not change appreciably during the course of the reaction. The concentration of the reactant in excess will remain almost constant. Thus the rate's dependence on B can be isolated and the rate law can be written

$$v = -\frac{d[B]}{dt} = k'[B] \quad \text{where} \quad k' = k \cdot [A] \quad (1)$$

Equation (1) represents the differential form of the rate law. Integration of this equation and evaluation of the integration constant C produces the corresponding integrated law.

Substituting $[B] = c$ into equation (1) yields:

$$-\frac{dc}{c} = k' \cdot dt \quad (2)$$

Integrating equation (2) gives:

$$\ln c = -k' \cdot t + C \quad (3)$$

The constant of integration C can be evaluated by using boundary conditions. At $t = 0$ the concentration of B is c_0 .

Therefore

$$C = \ln c_0 \quad (4)$$

Accordingly is obtained:

$$\ln c = \ln c_0 - k' \cdot t \quad \text{or} \quad c = c_0 \cdot e^{-k' \cdot t} \quad (5)$$

If the decrease in concentration of B is followed by photometric measurement the **Beer' Law** must be taken into account.

Combining equation (4) and Beer' Law

$$A = \log \frac{P_0}{P} = -\log T = \varepsilon \cdot c \cdot d \quad (6)$$

A = absorbance, ε = molar absorptivity with units of $L \cdot mol^{-1} \cdot cm^{-1}$
 c = concentration of the compound in solution, expressed in $mol \cdot L^{-1}$
 P_0 = radiant power for radiation entering, P = radiant power for radiation leaving

gives the relationship between k' and $\ln A$:

$$\ln A = -k' \cdot t + \ln c_0 + \ln(\varepsilon \cdot d) \quad \text{or} \quad \ln A = -k' \cdot t + C \quad (7)$$

One needs only monitor the relative concentration of B as a function of time to obtain the **pseudo-first order rate constant** k' . The value of k' can then be divided by the known, constant concentration of the excess compound to obtain the true constant second order k :

$$k = \frac{k'}{[A]_r} \quad (8)$$

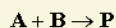
The **pseudo-first order rate constant** k' can be also determined from the **half-life** $t_{1/2}$:

$$k' \cdot t_{1/2} = \ln \frac{c_0}{c_0/2} \quad \text{or} \quad k' = \frac{\ln 2}{t_{1/2}} \quad (9)$$

Second Order Reaction

The rate of a second order reaction is proportional to either the concentration of a reactant squared, or the product of concentrations of two reactants.

For the general case of a reaction between A and B , such that



the rate of reaction will be given by

$$-\frac{d[A]}{dt} = k \cdot [A][B] \quad (1)$$

1. Initial concentrations of the two reactants are equal:

Equation (1) can be written as:

$$-\frac{d[A]}{dt} = k \cdot [A]^2 \quad (2)$$

Separating the variables and integrating gives:

$$\frac{1}{[A]} = kt + C \quad (3)$$

With the condition that $[A] = [A]_0$ at $t = 0$ the constant of integration C becomes equal to $1/[A]_0$.

Thus the second order integrated rate equation is

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad (4)$$

A plot of $1/[A]$ vs t produces a straight line with slope k and intercept $1/[A]_0$. The plot should be linear up to a conversion of 50%, that is up to the point at which 50% of the reactant concentration is consumed.

2. Starting concentrations of the two reactants are different:

If $[A]_0$ and $[B]_0$ are different the variable x is used.

Equation (1) becomes

$$\frac{dx}{([A]_0 - x)([B]_0 - x)} = kdt \quad (5)$$

where $[A]_0 - x = [A]$, $[B]_0 - x = [B]$ and x is the decrease in the concentration of A and B.

Taking into account that the left side can be written as

$$\frac{1}{[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - x} - \frac{1}{[B]_0 - x} \right) \quad (6)$$

Integrating equation (5) gives

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0 - x}{[B]_0 - x} = kt + C \quad (7)$$

where C is the constant of integration.

Using the condition that $x = 0$, when $t = 0$, the value of C can be found

$$C = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0}{[B]_0} \quad (8)$$

and equation (7) becomes

$$\ln \frac{[A]_0 - x}{[B]_0 - x} = kt ([B]_0 - [A]_0) + \ln \frac{[A]_0}{[B]_0} \quad (9)$$

A plot of

$$\ln \frac{[A]_0 - x}{[B]_0 - x} \quad (10)$$

against t should be a straight line.

If the experimental method yields reactant concentrations rather than x , the equivalent form of the equation is

$$\ln \frac{[B]_0 [A]}{[A]_0 [B]} = kt ([B]_0 - [A]_0) \quad (11)$$

If equimolar amounts of A and B are converted, then $[A]$ can be expressed by the concentration of B .

If $[B] = x$, $[A] = [A]_0 - (x_0 - x)$

Provided that the initial concentration of A is twice the concentration of B equation (11) becomes

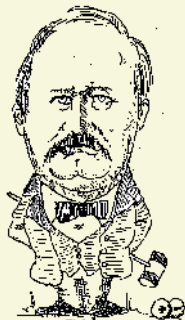
$$\ln \left[\frac{1}{2} \left(\frac{x_0}{x} + 1 \right) \right] = x_0 \cdot kt \quad (12)$$

Summary

Reaction Order	Differential Rate Law	Integrated Rate Law	Linear Plot	Slope of Linear Plot	Units of Rate Constant
0	$-d[A] / dt = k$	$[A] = [A]_0 - kt$	$[A]$ vs t	$-k$	$\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
1st	$-d[A] / dt = k [A]$	$[A] = [A]_0 e^{-kt}$	$\ln[A]$ vs t	$-k$	s^{-1}
2nd	$-d[A] / dt = k [A]^2$	$1/[A] = 1/[A]_0 + kt$	$1/[A]$ vs t	k	$\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

2. Arrhenius Equation

Arrhenius Equation



Svante Arrhenius

It is a well-known fact that raising the temperature increases the reaction rate. Quantitatively this relationship between the rate a reaction proceeds and its temperature is determined by the Arrhenius Equation:

$$k = A e^{-\frac{E_a}{RT}} \quad (1)$$

E_a = activation energy

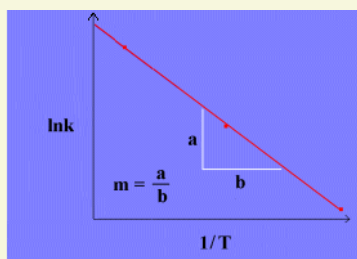
$R = 8.314 \text{ J/mol}\cdot\text{K}$

T = absolute temperature in Kelvins

A = frequency factor

The Arrhenius equation is often written in the logarithmic form:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (2)$$



Determination of E_a

A plot of $\ln k$ versus $1/T$ produces a straight line, from which the activation energy, E_a , can be determined because the slope is $-E_a/R$.

The y-intercept represents the value for $\ln A$.

An accurate determination of the activation energy requires at least three runs completed at different reaction temperatures.

"Two-Point" Arrhenius Equation

The "Two-Point" Equation provides a computational method to determine the activation energy for a given reaction from the experimental data found at two different reaction temperatures. The Arrhenius equations for two temperatures (T_1 and T_2) give two rate constants (k_1 and k_2):

$$\text{at } T_1: \quad \ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

$$\text{at } T_2: \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Combining the two Arrhenius equations yields

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3)$$

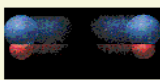
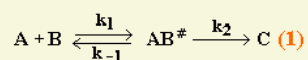
$$E_a = \frac{R T_1 T_2}{(T_1 - T_2)} \ln \frac{k_1}{k_2} \quad (4)$$



Henry Eyring

Both the **Arrhenius** and the **Eyring equation** describe the temperature dependence of reaction rate. In the strict sense, the **Arrhenius equation** may be applied only to gas reactions. The **Eyring equation** is used in gas, condensed and mixed phase reactions - all places where the simple **collision model** is not very helpful. The Arrhenius equation is founded on the empirical observation, that raising the temperature increases the rate of reaction. The **Eyring equation** is a theoretical construct, based on **transition state model**.

According to the '**transition state theory**' during a chemical reaction the reactants are getting over into an unsteady intermediate state.



Effective collision
Online Introductory Chemistry

When two particles **A** and **B** collide, due to collision energy a complex is formed. If the collision involves more than a certain amount of energy ('threshold energy'), the '**activated complex**' or '**transition state**' AB^{\ddagger} is formed, an unstable arrangement, in which bonds break and form to generate the products **C** or to degenerate back to the reactants **A** and **B**.

The concentration change of the complex AB^{\ddagger} can be described as follows:

$$\frac{d[AB^{\ddagger}]}{dt} = k_1 [A] \cdot [B] - k_{-1} [AB^{\ddagger}] - k_2 [AB^{\ddagger}] \quad (2)$$

Due to the equilibrium between the 'activated Complex' AB^{\ddagger} and the reactants **A** and **B**, the components $k_1 \cdot [A] \cdot [B]$ and $k_{-1} \cdot [AB^{\ddagger}]$ cancel out. Thus the reaction rate is directly proportional to the concentration of AB^{\ddagger} .

$$-\frac{d[AB^{\ddagger}]}{dt} = k_2 [AB^{\ddagger}] \quad (3)$$

k_2 is given by statistical mechanics:

$$k_2 = \frac{k_B \cdot T}{h} \quad (4)$$

$$k_B = \text{Boltzmann's constant } [1.381 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}]$$

$$h = \text{Planck constant } [6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}]$$

k_2 is called '**universal constant for a transition state**' ($\sim 6 \cdot 10^{12} \text{ sec}^{-1}$ at room temperature).

Additionally $[AB^{\ddagger}]$ can be derived from the quasi stationary equilibrium between AB^{\ddagger} and **A**, **B** by applying the mass action law:

$$[AB^{\ddagger}] = K^{\ddagger} \cdot [A] \cdot [B] \quad (5)$$

$K^{\ddagger} = \text{thermodynamic equilibrium constant}$

Due to the equilibrium that will be reached rapidly, the reactants and the activated complex decrease at the same rate. Therefore, considering both **equation (4)** and **(5)**, **equation (3)** become:

$$-\frac{d[AB^{\ddagger}]}{dt} = \frac{k_B \cdot T}{h} \cdot K^{\ddagger} \cdot [A] \cdot [B] \quad (6)$$

With consideration of the derived rate laws and by algebraic rearrangement, **equation (6)** can be rewritten:

$$k = \frac{k_B \cdot T}{h} \cdot K^{\ddagger} \quad (7)$$

Additionally thermodynamics gives a further representation of the equilibrium constant:

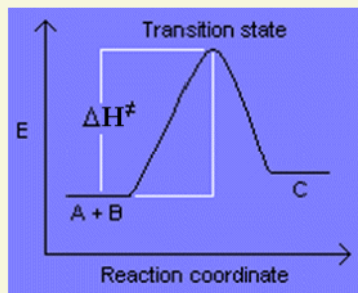
$$\Delta G^\# = -R \cdot T \cdot \ln K^\# \quad (8)$$

$$\Delta G^\# = \Delta H^\# - T \cdot \Delta S^\# \quad (9)$$

$\Delta G^\#$ = free activation enthalpy [$\text{kJ} \cdot \text{mol}^{-1}$]

$\Delta S^\#$ = activation entropy [$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$]

$\Delta H^\#$ = activation enthalpy [$\text{kJ} \cdot \text{mol}^{-1}$]



H is the amount of heat of a system with constant pressure. $\Delta H^\#$ is the enthalpy difference between the activated complex and the reactants A and B. It is called **activation enthalpy** (Fig. 1).

S is for the entropy, the extent of randomness or disorder in a system. The entropy difference between activated complex and the reactants is called **activation entropy** $\Delta S^\#$.

$\Delta G^\#$ is the **free activation enthalpy**. According to **equation (9)** $\Delta G^\#$ is **molar enthalpy** $\Delta H^\#$ minus the **product of the temperature** T (which is in kelvin) and the **change in entropy** $\Delta S^\#$. The general rule applies: A stabilization of the activated complex reduces the enthalpy difference $\Delta G^\#$ and increases the rate.

$\Delta G^\#$ represents the determining driving power for a reaction. The sign of $\Delta G^\#$ determines if a reaction is spontaneous or not.

Figure 1: Energy profile
 E: Potential energy
 Reaction coordinate: Bond length or bond angle
 Transition state: Maximum of energy in the path way,
 i.e. along the reaction coordinate

$$\begin{aligned} \Delta G^\# < 0 &\Rightarrow \text{reaction is spontaneous} \\ \Delta G^\# = 0 &\Rightarrow \text{system at equilibrium, no net change occurs} \\ \Delta G^\# > 0 &\Rightarrow \text{reaction is not spontaneous} \end{aligned}$$

Combining **Equation (8)** and the expression **(9)** and solving for **lnk** yields:

$$\ln K^\# = -\frac{\Delta H^\#}{R \cdot T} + \frac{\Delta S^\#}{T} \quad (10)$$

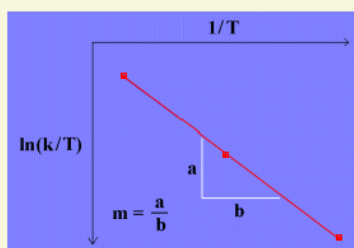
The **Eyring equation** is found by substituting **equation (10)** into **equation (7)**:

$$k = \frac{k_B \cdot T}{h} \cdot e^{-\frac{\Delta H^\#}{R T}} \cdot e^{\frac{\Delta S^\#}{R}} \quad (11)$$

Equation (11) is transformed into a linear expression:

$$\ln k = \ln \frac{k_B}{h} \cdot T - \frac{\Delta H^\#}{R} \cdot \frac{1}{T} + \frac{\Delta S^\#}{R} \quad (12)$$

$$\ln \frac{k}{T} = -\frac{\Delta H^\#}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\#}{R} \quad (13)$$



A plot of $\ln(k/T)$ versus $1/T$ will be a straight line with a slope of $m = -\Delta H^\ddagger / R$ (Fig. 2). ΔH^\ddagger can be calculated from the slope of this line. Multiplying $-m$ by $-R$ ($-8.314\text{J/mol}\cdot\text{K}$) yields ΔH^\ddagger .

Using the y-intercept

$$y(x=0) = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (14)$$

ΔS^\ddagger can be determined and thus is enabled the calculation of ΔG^\ddagger for the appropriate reaction temperatures according to equation (9).

Figure 2: Determination of ΔH^\ddagger

A comparison between the **Arrhenius equation** and the **Eyring equation** shows, that E_a and ΔH^\ddagger or $\ln A$ and ΔS^\ddagger are analog quantities. For mechanistical investigations the different activation parameters $E_a / \ln A$ or $\Delta H^\ddagger / \Delta S^\ddagger$ are used alternatively. The activation energy E_a is not exactly equal to the activation enthalpy ΔH^\ddagger , but is greater than it by a small amount (the difference is $R\cdot T$).

- Small values of E_a and $\Delta H^\ddagger \Rightarrow$ fast rate
- large values of E_a and $\Delta H^\ddagger \Rightarrow$ slow rate
- $\ln A$ small, corresponding to very negative values of $\Delta S^\ddagger \Rightarrow$ slow rate
- $\ln A$ large, corresponding to relatively positive values of $\Delta S^\ddagger \Rightarrow$ fast rate

Typical values for E_a and ΔH^\ddagger run from 20 to 150 [kJ / mol].

The study of the temperature dependence supplies the above all mechanistically important values $\ln A$ or ΔS^\ddagger , equivalent in their predicate strength.

- $\ln A$ small, corresponding to very negative values of ΔS^\ddagger (unfavorable)

The transition state is highly ordered in comparison to the ground state. This is generally the case, if on the way to the transition state, degrees of freedom (translational, rotational or vibrational) are frozen.

- $\ln A$ large, corresponding to relatively positive values of ΔS^\ddagger (favorable)

In comparison to the ground state the transition state is disordered. Translational, rotational or vibrational degrees of freedom are set free.

$\ln A$ and ΔS^\ddagger are sensible sensors for the status order of transition state.

Note:

Although the determination of the activation parameters must be performed accurately, it may not pretend an excessive accuracy. The values of the activation energy and activation enthalpy are rounded in publications to one decimal place. The value of activation entropy is to be specified basically with whole numbers. Values of entropies $\Delta S^\ddagger < \pm 10$ are written to one decimal place of accuracy. The value of $\ln A$ shall be expressed with an accuracy of two decimal places.

An accurate determination of the activation energy requires at least three runs completed at different reaction temperatures. If the data points in the plot of $\ln(k/T)$ versus $1/T$ (Fig. 2) do not lie exactly on a straight line, a linear regression analysis providing the 'line of best fit' will not increase the accuracy. If the plotted points deviate significantly from the straight line, the rate constant should be determined at a further reaction temperature, since each of the three data points can be false. Basically, it recommends to increase the accuracy of the measured values by improvement of the measuring method (accurate thermostating of reaction solutions). Sometimes the data points are positioned on a concave or convex curve. Most notably a secondary reaction is responsible for this behavior. The secondary reaction will have more or less importance, owing to the deviation of activation parameters with rising temperature. In this case the calculation of the activation parameters is senseless.