

# Arrhenius Equation

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The experimental observation that the rate of a chemical reaction increases with temperature raised an important question: *Why does the rate constant increase so rapidly with temperature?* Although the temperature coefficient provided a rough estimate of this effect, it could neither explain the molecular basis of the phenomenon nor predict the rate constant at different temperatures. In 1889, the Swedish chemist **Svante Arrhenius** answered this question by proposing a mathematical relationship between the rate constant and the absolute temperature. This relationship, known as the **Arrhenius equation**, is one of the fundamental equations of chemical kinetics and forms the basis for understanding the temperature dependence of reaction rates.

Arrhenius proposed that only those molecules possessing energy equal to or greater than a certain minimum value, called the **activation energy**, are capable of undergoing a chemical reaction. At any given temperature, only a fraction of the molecules has sufficient energy to overcome this energy barrier. As the temperature increases, this fraction increases rapidly, causing the rate constant and, consequently, the reaction rate to increase.

## Mathematical Expression

The Arrhenius equation is expressed as

$$k = Ae^{-E_a/RT}$$

where

- $k$  = rate constant of the reaction
- $A$  = Arrhenius constant or frequency factor
- $E_a$  = activation energy of the reaction ( $\text{J mol}^{-1}$ )
- $R$  = universal gas constant  
( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
- $T$  = absolute temperature (K)
- $e$  = base of the natural logarithm

The exponential term,

$$e^{-E_a/RT}$$

represents the fraction of molecules that possess sufficient energy to overcome the activation energy barrier. As the temperature increases, the value of this exponential term increases rapidly, resulting in a larger value of the rate constant.

## Significance of the Frequency Factor

The constant  $A$ , commonly known as the **frequency factor** or **pre-exponential factor**, represents the maximum possible rate constant that would be obtained if every molecular collision were effective. It depends on the frequency of collisions between reacting molecules and the probability that these molecules collide with the proper orientation required for bond breaking and bond formation. Therefore, the value of  $A$  is influenced not only by the number of collisions but also by the molecular structure of the reactants.

## Physical Significance of Activation Energy

Activation energy is the minimum amount of energy that reacting molecules must acquire before they can be converted into products. During a chemical reaction, reactant molecules first absorb energy to form a short-lived, unstable intermediate known as the activated complex or transition state. Once this energy barrier is crossed, the activated complex decomposes to form the products. A reaction having a high activation energy proceeds slowly because only a small fraction of molecules possesses sufficient energy for reaction, whereas a reaction with a low activation energy occurs much more rapidly.

## Logarithmic Form of the Arrhenius Equation

Taking the natural logarithm of the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

gives

$$\ln k = \ln A - \frac{E_a}{RT}$$

Converting the equation into common logarithmic form,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

This equation is particularly useful because it represents the equation of a straight line.

$$y = mx + c$$

Comparing the two equations,

$$\log k = \log A - \frac{E_a}{2.303R} \left( \frac{1}{T} \right)$$

it follows that a plot of  $\log k$  against  $1/T$  gives a straight line having:

- Slope  $= -\frac{E_a}{2.303R}$
- Intercept  $= \log A$

This graphical method is extensively used to determine the activation energy of a reaction from experimental data.



## Factors Affecting the Rate Constant According to the Arrhenius Equation

- An increase in temperature increases the value of the rate constant.
- A larger activation energy decreases the value of the rate constant.
- A larger frequency factor increases the probability of effective collisions and therefore increases the rate constant.

## Applications of the Arrhenius Equation

- Determination of activation energy from experimental rate constants.
- Prediction of reaction rates at different temperatures.
- Study of reaction mechanisms.
- Estimation of shelf life and stability of pharmaceuticals.
- Optimization of industrial chemical processes.
- Investigation of catalytic reactions.

## Limitations

- The equation assumes that the activation energy remains constant over the temperature range studied.
- It does not explain the molecular details of the activated complex.
- For highly complex reactions, deviations from Arrhenius behaviour may be observed.

The Arrhenius equation established the first quantitative relationship between reaction rate and temperature and remains one of the most significant achievements in chemical kinetics. However, the equation does not explain how reactants are transformed into products at the molecular level. This limitation was overcome by the development of **Collision Theory** and later by **Transition State Theory**, which provide a more detailed description of the reaction mechanism.