The pre-exponential factor \((A)\) is part of the Arrhenius equation, which was formulated by the Swedish chemist Svante Arrhenius in 1889. The pre-exponential factor is also known as the frequency factor, and represents the frequency of collisions between reactant molecules. Although often described as temperature independent, it is actually dependent on temperature because it is related to molecular collision, which is a function of temperature.

**Temperature Dependence of Reactions**

The units of the pre-exponential factor vary depending on the order of the reaction and thus on the rate constant. In a first order reaction, the units of the pre-exponential factor are reciprocal seconds. Because the pre-exponential factor depends on frequency of collisions, its related to collision theory and transition state theory.

\[
\text{Arrhenius Equation:} \\
K = Ae^{-\frac{E_a}{RT}} \\
\uparrow \\
\text{Pre-exponential factor}
\]

The Arrhenius equation introduces the relationships between rate and \((A)\), \((E_a)\) and \((T)\), where \((A)\) is the pre-exponential factor, \((E_a)\) is the activation energy, and \((T)\) is the temperature. The pre-exponential factor, \((A)\), is a constant that can be derived experimentally or numerically. It is also called the frequency factor, and describes the number of times two molecules collide. In empirical settings, the pre-exponential factor is considered constant.

When dealing with the collision theory, the pre-exponential factor is defined as \((Z)\) and its equation can be derived by considering the factors that affect the frequency of collision for a given molecule. Consider the most elementary bimolecular reaction:

\[
\text{(A + A } \rightarrow \text{ Product)}
\]

An underlying factor to the frequency of collisions is the space or volume in which this reaction is allowed to occur. Intuitively, it makes sense for the frequency of collisions between two molecules to be dependent upon the dimensions of their respective containers. By this logic, \(Z\) is defined the following way:

\[
Z = (\text{Volume of the cylinder} \ast \text{Density of the particles}) / \text{time}
\]

Using this relationship, an equation for the collision frequency, \((Z)\), of molecule \((A)\) with \((A)\) can be derived:

\[
[Z_{AA} = 2N^2Ad^2 \sqrt{\frac{\pi k_B T}{m_a}}]
\]

For a more complex collision, such as one between \((A)\) and \((B)\):

\[
[A + B \rightarrow \text{Product}]
\]
The same reasoning is used to derive the following equation for the collision frequency, \(Z\), of molecule \(A\) and \(B\):

\[
Z_{AB} = N_AN_Bd^2\sqrt{8\frac{k_BT}{\mu}}
\]

Substituting the collision factor back into the original Arrhenius equation yields:

\[
k = Z_{AB}e^{\frac{-E_a}{RT}}
\]

\[
k = Z_{AB} = N_A, N_B, d^2 \sqrt{8\frac{k_BT}{\mu}}, e^{\frac{-E_a}{RT}}
\]

This equation produces a rate constant with the standard units of \(\frac{M}{s}\); however, on a molecular level, a rate constant with molecular units would be more useful. To obtain this constant, the rate is divided by \(N_A, N_B\). This produces a rate constant with units \(\frac{m^3}{mol \cdot s}\) and provides the following equation:

\[
k = Z_{AB} e^{\frac{-E_a}{RT}}
\]

Divide both sides by \(N_A N_B\):

\[
\frac{k}{N_AN_B} = d^2\sqrt{8\frac{k_BT}{\mu}}e^{\frac{-E_a}{RT}}
\]

\(Z_{AB}\) becomes \(z_{AB}\):

\[
\frac{Z_{AB}}{N_AN_B} = z_{AB}
\]

Substituting back into the Arrhenius equation,

\[
k = z_{AB}e^{\frac{-E_a}{RT}}
\]

The pre-exponential factor is now defined within the collision theory as the following:

\[
d^2\sqrt{8\frac{k_BT}{\mu}}
\]

A and \(Z\) are practically interchangeable terms for collision frequency. Often times however, when the term is determined experimentally, \(A\) is the preferred variable and when the constant is determined mathematically, \(\sqrt{Z}\) is the variable more often used. The derivation for \(Z\), while mostly accurate, ignores the steric effect of molecules. For a reaction to occur, two molecules must collide in the correct orientation. Not every collision results in the proper orientation, and thus some do not yield a corresponding product.

To account for this steric effect, the variable \(P\), which represents the probability of two atoms colliding with the proper orientation, is introduced. The Arrhenius equation is as follows:

\[
k = Pze^{\frac{-E_a}{RT}}
\]

The probability factor, \(P\), is very difficult to assess and still leaves the Arrhenius equation imperfect.
Transition State Theory Pre-exponential Theory

The collision theory deals with gases and neglects to account for structural complexities in atoms and molecules. Therefore, the collision theory estimation for probability is not accurate for species other than gases. The transition state theory attempts to resolve this discrepancy. It uses the foundations of thermodynamics to give a representation of the most accurate pre-exponential factor that yields the corresponding rate. The equation is derived through laws concerning Gibbs free energy, enthalpy and entropy:

$$k = \frac{k_bT}{h} e^{\frac{\Delta S^o}{R}} e^{\frac{-\Delta H^o}{RT}}(M^{1-m})$$

Table 1: Pre-exponential factor table. The following table summarizes the three exponential factors discussed, as well as their types:

<table>
<thead>
<tr>
<th>Factor</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Empirical</td>
</tr>
<tr>
<td>$\sqrt{\frac{8k_bT}{\mu}}$$d^2_{AB}$</td>
<td>Collision Theory</td>
</tr>
<tr>
<td>$\frac{k_bT}{h}$</td>
<td>Transition State Theory</td>
</tr>
</tbody>
</table>

The pre-exponential factor is a function of temperature. As indicated in Table 1, the factor for the collision theory and the transition state theory are both responsive to temperature changes. The collision theory factor is proportional to the square root of $\langle T \rangle$, whereas that of the transition state theory is proportional to $\langle T \rangle$. The empirical factor is also sensitive to temperature. As temperature increases, molecules move faster; as molecules move faster, they are more likely to collide and therefore affect the collision frequency, $\langle A \rangle$.

Sources


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