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Suppose that we have a container filled with gas particles A. We can determine the collision frequency for a single molecule, Z_A, by freezing all other atoms within the container and count the number of collisions within a period of time.[1] The number of collisions can be calculated using the following formula.

$$Z_A = \frac{\text{Volume of Collisional Cylinder} \times \text{Density}}{\text{Time}} \tag{1}$$

This equation can be later generalized to find the collision frequency for two different types of molecules, Z_{AB}

3.1.1 Volume of Collision Cylinder

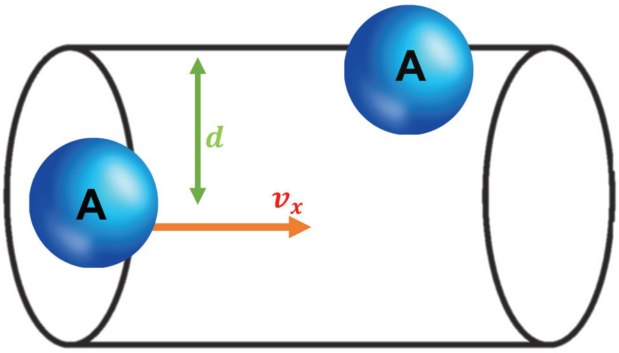

Figure 3: Collision Cylinder of Atom A

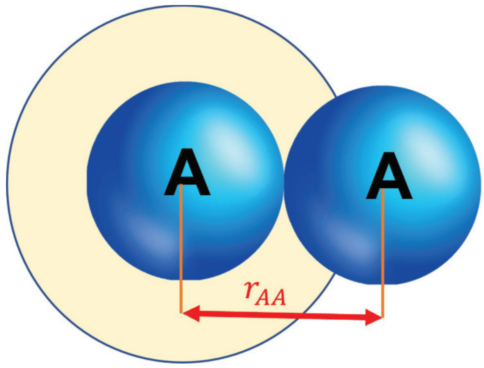

Figure 4: Collision Cross Section of atom A and B

The Collision Cylinder (**Figure 3**) can be viewed as the volume whose cross-sectional area – the Collision Cross Section – contains the center of the second particle if the two particles are aligned to collide in the future. This can be better visualized in the **Figure 4**. Simply put, it is a volume swept out by the particle A in a time period Δt.[3]

Note that although a collision will like likely change the direction of the moving particle, this does not affect the volume of the Collision Cylinder nor the density within the system. Thus, the equation will hold true from one collision to the next.

We can find the area of the collision cross section with the area formula of a circle:

$$\sigma_{AA} = \pi r_{AA}^2 = \pi(2r_A)^2 \tag{2}$$

The sum of the radius of two identical spheres can also be expressed as their diameter, d_A:

$$\sigma_{AA} = \pi r_{AA}^2 = \pi(d_A)^2 \tag{3}$$

Using equation 3, the volume of the collision cylinder is given by:

$$\begin{aligned} V &= \sigma_{AA} \cdot c_A \cdot \Delta t \\ &= \pi(d_A)^2 \cdot c_A \cdot \Delta t \end{aligned} \tag{4}$$

where c_A is the mean speed of particle A and Δt is an arbitrary amount of time.

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3.1.2 Collision Frequency for a Single Particle A

Knowing the volume of the collision cylinder, the next parameter that needs to be taken into account is the number density of the molecules within the system, that is the number of a specific type of molecule within a unit volume. This will let us know the expected number of collisions within a time frame. The number density can be simply computed as:

Bemærk, N_A er ikke Avogadros tal

$$\rho = \frac{N_A}{V} \tag{5}$$

where N_A is the number of particles A within the system and V is the volume of our container.

Plugging the equations 4 and 5 into the equation 1 yields the collision frequency of a single particle A.

$$\begin{aligned} Z_A &= \frac{\pi(d_A)^2 \cdot c_A \cdot \Delta t \cdot \frac{N_A}{V}}{\Delta t} \\ &= \frac{\pi(d_A)^2 \cdot c_A \cdot N_A}{V} \end{aligned} \tag{6}$$

3.1.3 Collision Frequency for all Particles A

Now, every particle in the container starts moving again. It is possible to compute the collision frequency of all the A molecules, Z_{AA}, through the following relation:

$$Z_{AA} = \frac{1}{2} \cdot Z_A \cdot \frac{N_A}{V} \tag{7}$$

This relation accounts for the fact that every A molecule in the system can collide with another molecule in the same mechanism described above, thus we multiply it with the number density of A. Further, every collision is counted twice, thus we half the number.

Plugging the equation 6 into 7 yields:

$$Z_{AA} = \frac{\pi(d_A)^2 \cdot c_A}{2} \cdot \left(\frac{N_A}{V}\right)^2 \tag{8}$$

3.1.4 Collision System Between Different Types of Molecules

The ultimate goal of the pre-exponential factor model is to build a general equation accounting for the collision frequency between two types of reactants, Z_{AB}. Namely, the equation should describe an elementary reaction of the type:

coll-frekvens målt i antal molek (A og B), der kolliderer. Et sammenstød af en A og en B tæller med 1 til frekvensen

$$A_{(g)} + B_{(g)} \rightarrow \text{product}$$

The equation 8 can easily be modified to account for the change. We need only to modify the following elements:

1. The collisional cross section should take into account the radius of both particles. Thus d_A should be replaced with $r_A + r_B$.

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2. The number of particles A and particles B could differ significantly within the container. To find the probability of a collision between these two types of particles, the particle density within the collisional cylinder should be replaced with the number density of the second particle, $\frac{N_B}{V}$.

3. There is no need to divide the collision frequency by two (look at equation 7) since we are now only counting the frequency of an A molecule striking B and not vice versa.

4. Since we are considering a two bodied system, the mean speed of particle A should be replaced by the relative speed of particles A and B, c_{AB}.

Rewriting equation 8 with the above modifications gives the following result:

$$Z_{AB} = \pi(r_A + r_B)^2 \cdot c_{AB} \cdot \frac{N_A N_B}{V^2} \tag{9}$$

Furthermore, c_{AB} could be expanded using the formula of mean gas particle velocity.

Dette er en af de tre typer middel-hastighed, udregnet i wiki-artiklen Maxwell -Boltzmanndistribution,

$$c = \sqrt{\frac{8k_BT}{\pi m}}$$

However, since we are converting a two bodied system to a one-body system, it is important to use the reduced mass of particles A and B. The reduced mass is found by:[4]

reduced mass er forklaret i 5.2 i McQuarrie and Simon

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$$

Plugging equation 10 into 9 yields the desired result for collision frequency:

$$Z_{AB} = \frac{N_A N_B}{V^2}(r_A + r_B)^2 \sqrt{\frac{8\pi k_BT}{\mu_{AB}}} \tag{11}$$

Z_AB er kollisions-frekvens målt i antal molek (et A og et B tæller 1), der støder sammen. A_AB er frekvensen målt i antal mol af fx A, der er involveret i sammenstød. Så Z_AB / avogradro = A_AB

Finally, we can find the collision frequency as a function of the concentration of both reactants, A_{AB}, rather than as individual molecules. Thus, we divide both sides of the equation by N_{avo}^2 where N_{avo} is the Avogadro's number and substitute $\frac{n_A}{V}$ by C_A and $\frac{n_B}{V}$ by C_B:

n_A=N_A/avogadros tal må være antal mol af A, tilsv B. mol / V er koncentrationen målt i mol

C_A betegnes også [A]

$$A_{AB} = N_{avo} C_A C_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_BT}{\mu_{AB}}} \tag{12}$$

3.2 Pre-Exponential Factor

Now that we have developed a formula for the collision frequency for bimolecular gases reactions, we can use the equation to find the pre-exponential factor by comparing with the reaction rate predicted by classical rate law and the Arrhenius equation. In other words, we isolate the pre-exponential term equivalent in the collision frequency formula.

3.2.1 Reaction Rate According to the Collision Theories

According to collision theories, the rate of a chemical reaction will directly be affected by the following 3 factors:

1. The ratio of particles possessing a sufficient amount of kinetic energy. When colliding, this energy is transformed to potential energy in order to bypass the activation energy barrier, E_a.

2. The number of collisions within a unit time period.

3. The particles collide in the exact geometry in such a way that their electrons cloud interact with one another. This coefficient is called the orientation factor. [1]

The ratio of molecules with sufficient kinetic energy is equal to the exponential term while the number of collisions is given by the equation 12 as the collision frequency. Taking these factors into consideration, the rate of a bimolecular reaction, $\frac{-dC_A}{dt}$ is expressed as:

$$\frac{-dC_A}{dt} = N_{avo}C_AC_B(r_A + r_B)^2\sqrt{\frac{8\pi k_BT}{\mu_{AB}}} \cdot e^{\frac{-E_a}{RT}} \tag{13}$$

Note that we can also obtain the reaction rate using classical the rate law for elementary reactions:

$$\frac{-dC_A}{dt} = kC_AC_B \tag{14}$$

Substituting the rate constant k with the Arrhenius equation, we get:

$$\frac{-dC_A}{dt} = Ae^{\frac{-E_a}{RT}} \cdot C_AC_B \tag{15}$$

Equating equations 13 and 15 and cancelling identical terms yields the desired result of our model:

$$Ae^{\frac{-E_a}{RT}} \cdot C_AC_B = N_{avo}C_AC_B(r_A + r_B)^2\sqrt{\frac{8\pi k_BT}{\mu_{AB}}} \cdot e^{\frac{-E_a}{RT}}$$
$$A = N_{avo}(r_A + r_B)^2\sqrt{\frac{8\pi k_BT}{\mu_{AB}}}$$

Mathematical Model of the Pre-exponential Factor using Collision Theory:

$$A = N_{avo}(r_A + r_B)^2\sqrt{\frac{8\pi k_BT}{\mu_{AB}}} \tag{16}$$

3.3 Limitations of the Model

Although the mathematical model of the pre-exponential factor offers a general approximation, it often does not give an exact value. In fact, in some cases (as listed below), the errors add up to one another, making the gap between our approximate and the empirical value quite significant. Even small variations in the particles' characteristics - including their mass and radius - may have an enormous influence on the final value of the pre-exponential factor. All these errors mainly arise from the limits of the collision theories, which do not provide a detailed account of the mechanism during a reaction. The following is a list of assumptions we made to simplify the problem:[2]

[1]The orientation factor will not be discussed in this demonstration as it is highly dependent on the type of reactant and cannot be generalized in by a simple formula.

1. It is assumed that all particles behave like hard spheres with a defined radius and a defined position. However, in reality, atoms react when their electron clouds come sufficiently close together to interact with one another. The electron cloud is consisted of a probability range, which means there is not a precisely defined distance below which atoms react.

2. It is assumed that every collision in which the particles possess sufficient kinetic energy will undergo chemical transformation. This statement does not reflect the reality, as molecules must imperatively hit one another in the precise geometry to form an activated complex.

3. In the collision theory, only the kinetic energy of particles is considered, while rotation and vibration energies are ignored.

Furthermore, this model has a restrained scope of usage, as it can only be applied to bimolecular reactions with all reactants in a gaseous state. Particles behave slightly differently in aqueous solutions, as they will have a different average velocity. The transition state theories generally offer a quantitative understanding of chemical reactions in solutions.

4 Conclusion

The Arrhenius equation proved to be an essential tool in understanding various molecular aspects of chemical reactions including activation energy requirements and temperature dependence. Further modelling of the pre-exponential factor using collision theory unveils its dependence on temperature, atomic radius and gas speed. It is important to note, however, that the collision theory does not offer a precise account of the reaction mechanism because several assumptions were made to simplify the problem. Advanced modelling will be necessary to understand chemical reactions in deeper detail. Nevertheless, the results shown in this paper can be combined with other formulas and are essential for both basic reaction analysis and for advanced kinetic modelling. These advances along with improving computational methods have made possible the optimization of existing chemical reactions and the development of new industrial processes.

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