Collisional Frequency is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system.

**Background and Overview**

To fully understand how the collisional frequency equation is derived, consider a simple system (a jar full of helium) and add each new concept in a step-by-step fashion. Before continuing with this topic, it is suggested that the articles on collision theory and collisional cross section are reviewed, as these topics are essential to understanding collisional frequency. The equation for collisional frequency is the following:

\[
\langle Z_{AB} \rangle = N_A N_B \left( r_A + r_B \right)^2 \sqrt{ \frac{8 \pi K_B T}{\mu_{AB}}} 
\]

Also, although technically these statements are false, the following assumptions are used when deriving and calculating the collisional frequency:

- All molecules travel through space in straight lines.
- All molecules are hard, solid spheres.
- The reaction of interest is between only two molecules.
- Collisions are hit or miss only. They occur when distance between the center of the two reactants is less than or equal to the sum of their respective radii. Even if the two molecules barely miss each other, it is still considered a complete miss. The two molecules do not interact (in reality, their electron clouds would interact, but this has no bearing on the equation).

**Single Molecule Moving**

In determining the collisional frequency for a single molecule, \(\langle Z_i \rangle\), picture a jar filled with helium atoms. These atoms collide by hitting other helium atoms within the jar. If every atom except one is frozen and the number of collisions in one minute is counted, the collisional frequency (per minute) of a single atom of helium within the container could be determined. This is the basis for the equation.

\[
\langle Z_i \rangle = \frac{\text{(Volume of Collisional Cylinder)}}{\text{Density}(\text{Cylinder})(\text{Time})}
\]
While the helium atom is moving through space, it sweeps out a collisional cylinder, as shown above. If the center of another helium atom is present within the cylinder, a collision occurs. The length of the cylinder is the helium atom's mean relative speed, \(\sqrt{2}\langle c \rangle\), multiplied by change in time, \(\Delta t\). The mean relative speed is used instead of average speed because, in reality, the other atoms are moving and this factor accounts for some of that. The area of the cylinder is the helium atom's collisional cross section.

Although collision will most likely change the direction an atom moves, it does not affect the volume of the collisional cylinder, which is due to density being uniform throughout the system. Therefore, an atom has the same chance of colliding with another atom regardless of direction as long as the distance traveled is the same.

\[
\text{(Volume of Collisional Cylinder) } = \sqrt{2}\pi d^2 \langle c \rangle \Delta t
\]

**Density**

Next, account must be taken of the other atoms that are moving that helium can hit; which is simply the density \(\rho\) of helium within the system. The density component can be expanded in terms of N and V. N is the number of atoms in the system, and V is the volume of the system. Alternatively, the density in terms of pressure (relating pressure to volume using the perfect gas law equation, \(PV = nRT\):

\[
\rho = \left(\frac{N}{V}\right) = \left(\frac{\rho N_A}{V}\right) = \left(\frac{\rho N_A}{RT}\right) = \left(\frac{\rho}{kT}\right)
\]

**The Full Equation**

When you substitute in the values for \(Z_i\), the following equation results:

\[
\left(Z_i = \frac{\sqrt{2}\pi d^2 \langle c \rangle \Delta t}{\Delta t}\right)\left(\frac{N}{V}\right)
\]

Cancel \(\Delta t\):

\[
Z_i = \sqrt{2}\pi d^2 \langle c \rangle \left(\frac{N}{V}\right)
\]
All Molecules Moving System: \((Z_{ii})\)

Now imagine that all of the helium atoms in the jar are moving again. When all of the collisions for every atom of helium moving within the jar in a minute are counted, \(Z_{ii}\) results. The relation is thus:

\[
[Z_{ii}] = \dfrac{1}{2} Z_{i} \left(\dfrac{N}{V}\right)
\]

This expands to:

\[
[Z_{ii}] = \sqrt{2} \pi d^{2} \langle c \rangle \left(\dfrac{N}{V}\right)^{2}
\]

System With Collisions Between Different Types of Molecules: \((Z_{AB})\)

Consider a system of hydrogen in a jar:

\[
[H_{A} + H_{BC}] \leftrightarrow [H_{AB} + H_{C}]
\]

In considering hydrogen in a jar instead of helium, there are several problems. First, the \(H_{A}\) ions have a smaller radius than the \(H_{BC}\) molecules. This is easily solved by accounting for the different radii which changes \(d(2)^{2}\) to \(\left(r_{A} + r_{B}\right)^{2}\).

The second problem is that the number of \(H_{A}\) ions could be much different than the number of \(H_{BC}\) molecules. So we expand \(\sqrt{2} \pi d^{2} \langle c \rangle \left(\dfrac{N}{V}\right)^{2}\) to account for the number of both reacting molecules to get \(N_{A}N_{B}\). Because two reactants are considered, \(Z_{ii}\) becomes \(Z_{AB}\), and the two changes are combined to give the following equation:

\[
[Z_{AB}] = N_{A}N_{B} \pi \left(r_{A} + r_{B}\right)^{2} \langle c \rangle
\]

Mean speed, \(\langle c \rangle\), can be expanded:

\[
\langle c \rangle = \sqrt{\dfrac{8k_{B}T}{\pi m}}
\]

This leads to the final change to the collisional frequency equation. Because two different molecules must be taken into account, the equation must accommodate molecules of different masses (\(m\)). So, mass (\(m\)) must be converted to reduced mass, \(\mu_{AB}\), converting a two bodied system to a one bodied system. Now we substitute \(\langle c \rangle\) in the \(Z_{AB}\) equation to obtain:

\[
[Z_{AB}] = N_{A}N_{B} \pi \left(r_{A} + r_{B}\right)^{2} \sqrt{\dfrac{8\pi k_{B}T}{\mu_{AB}}}
\]

Cancel \(\pi\):

\[
[Z_{AB}] = N_{A}N_{B} \left(r_{A} + r_{B}\right)^{2} \sqrt{\dfrac{8k_{B}T}{\mu_{AB}}}
\]

with

- \(N_{A}\) is the number of A molecules in the system
- \(N_{B}\) is the number of B molecules in the system
• \(r_a\) is the radius of molecule A
• \(r_b\) is the radius of molecule B
• \(k_B\) is the Boltzmann constant \(k_B = 1.380 \times 10^{-23}\) Joules Kelvin
• \(T\) is the temperature in Kelvin
• \(\mu_{AB}\) is the reduced mass found by using the equation \(\mu_{AB} = \frac{m_A m_B}{m_A + m_B}\)

Variables that affect Collisional Frequency

• **Temperature**: As is evident from the collisional frequency equation, when temperature increases, the collisional frequency increases.

• **Density**: From a conceptual point, if the density is increased, the number of molecules per volume is also increased. If everything else remains constant, a single reactant comes in contact with more atoms in a denser system. Thus if density is increased, the collisional frequency must also increase.

• **Size of Reactants**: Increasing the size of the reactants increases the collisional frequency. This is directly due to increasing the radius of the reactants as this increases the collisional cross section. This in turn increases the collisional cylinder. Because radius term is squared, if the radius of one of the reactants is doubled, the collisional frequency is quadrupled. If the radii of both reactants are doubled, the collisional frequency is increased by a factor of 16.

Problems

1. If the temperature of the system was increased, how would the collisional frequency be affected?
2. If the masses of both the reactants were increased, how would the collisional frequency be affected?
3. 0.4 moles of N\(_2\) gas (molecular diameter= 3.8x10\(^{-10}\) m and mass= 28 g/mol) occupies a 1-liter (0.001m\(^3\)) container at 1 atm of pressure and at room temperature (298K)

   a) Calculate the number of collisions a single molecule makes in one second.(hint use Z\(_i\))

   b) Calculate the binary collision frequency.(hint use Z\(_ii\))

References

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