

6.1.4: Collision Frequency

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.

In determining the collisional frequency for a single molecule, Z_i , 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.

$$Z_i = \frac{(\text{Volume of Collisional Cylinder})(\text{Density})}{\text{Time}}$$

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, Δt . 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](#).

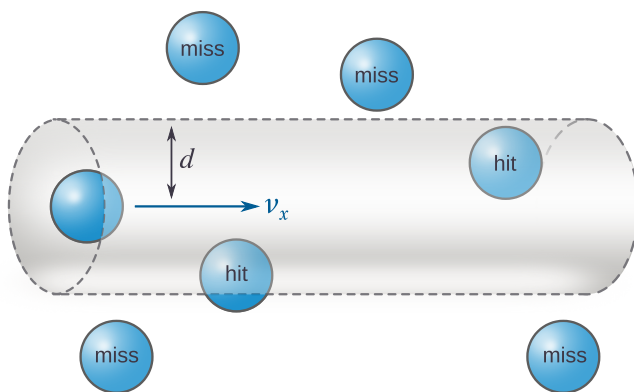


Figure 6.1.4.1: Collisional Cylinder. (CC BY 4.0; Ümit Kaya via LibreTexts)

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 ρ 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:

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

Cancel Δt :

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

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:

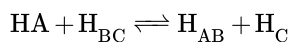
$$Z_{ii} = \frac{1}{2} Z_i \left(\frac{N}{V} \right)$$

This expands to:

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

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

Consider a system of hydrogen in a jar:



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 to $(r_A + r_B)^2$.

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 $\frac{\sqrt{2}}{2} \left(\frac{N}{V} \right)^2$ 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:

$$Z_{AB} = N_A N_B \pi (r_A + r_B)^2 \langle c \rangle$$

Mean speed, $\langle c \rangle$, can be expanded:

$$\langle c \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

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, μ_{AB} , converting a two bodied system to a one bodied system. Now we substitute $\langle c \rangle$ in the Z_{AB} equation to obtain:

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \pi \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$$

Cancel π :

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}}$$

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
- μ_{AB} is the reduced mass found by using the equation $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

The following assumptions are used when deriving and calculating the collisional frequency:

1. All molecules travel through space in straight lines.
2. All molecules are hard, solid spheres.
3. The reaction of interest is between only two molecules.
4. 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 (in reality, their electron clouds would interact).

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.

Exercise 6.1.4.1

If the temperature of the system was increased, how would the collisional frequency be affected?

Exercise 6.1.4.2

If the masses of both the reactants were increased, how would the collisional frequency be affected?

Exercise 6.1.4.3

0.4 moles of N_2 gas (molecular diameter = 3.8×10^{-10} m and mass = 28 g/mol) occupies a 1-liter ($0.001 m^3$) container at 1 atm of pressure and at room temperature (298 K)

- 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

1. Atkins, Peter and Julio de Paula. Physical Chemistry for the Life Sciences. 2006. New York, NY: W.H. Freeman and Company. pp.282-288, 290
2. Atkins, Peter. Physical Chemistry: Sixth Edition. 2000. New York, NY: W.H. Freeman and Company. pp.29,30
3. Atkins, Peter. Concepts in Physical Chemistry. 1995. New York, NY: W.H. Freeman and Company. pp.64

6.1.4: Collision Frequency is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by Keith Dunaway & Imteaz Siddique.