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collision theory

Various collision theories, dealing with the frequency of collision between reactant molecules, have been put forward. In the earliest theories reactant molecules were regarded as hard spheres, and a collision was considered to occur when the distance d between the centres of two molecules was equal to the sum of their radii. For a gas containing only one type of molecule, **A**, the collision density is given by simple collision theory as:

$$Z_{AA} = \frac{\sqrt{2}\,\pi\,\sigma^2\,u\,{N_A}^2}{2}$$

Here N_A is the number density of molecules and u is the mean molecular speed, given by kinetic theory to be $\sqrt{\frac{8\,k_B\,T}{\pi\,m}}$, where m is the molecular mass, and $\sigma = \pi\,{d_{AA}}^2$. Thus:

$$Z_{AA} = 2\,{N_A}^2\,\sigma^2\sqrt{\frac{\pi\,k_B\,T}{m}}$$

The corresponding expression for the collision density Z_{AB} for two unlike molecules **A** and **B**, of masses m_A and m_B is:

$$Z_{AB} = N_A\,N_B\,\sigma^2\sqrt{\frac{\pi\,k_B\,T}{\mu}}$$

where μ is the reduced mass $\frac{m_A\,m_B}{m_A + m_B}$, and $\sigma = \pi\,{d_{AB}}^2$. For the collision frequency factor these formulations lead to the following expression:

$$z_{AA} \text{ or } z_{AB} = L\,\sigma^2\sqrt{\frac{8\,\pi\,k_B\,T}{\mu}}$$

where L is the Avogadro constant. More advanced collision theories, not involving the assumption that molecules behave as hard spheres, are known as generalized kinetic theories.

Source:
PAC, 1996, *68*, 149 *(A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996))* on page 160

