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:

$$Z_{AA} = \tfrac{1}{2}\sqrt{2}\,\pi\sigma^2 u N_A^2$$

Here N_A is the number density of molecules and u is the mean molecular speed, given by kinetic theory to be $(8k_BT/\pi m)^{1/2}$, where m is the molecular mass, and $\sigma = \pi d_{AA}^2$. Thus:

$$Z_{AA} = 2N_A^2\sigma^2(\pi k_B T/m)^{1/2}$$

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

$$Z_{AB} = N_A N_B \sigma^2 (\pi k_B T/\mu)^{1/2}$$

where μ is the reduced mass $m_A m_B/(m_A+m_B)$, and $\sigma = \pi d_{AB}^2$.

For the collision frequency factor these formulations lead to the following expression:

$$z_{AA} \text{ or } z_{AB} = L\sigma^2(8\pi k_B T/\mu)^{1/2}$$

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.

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