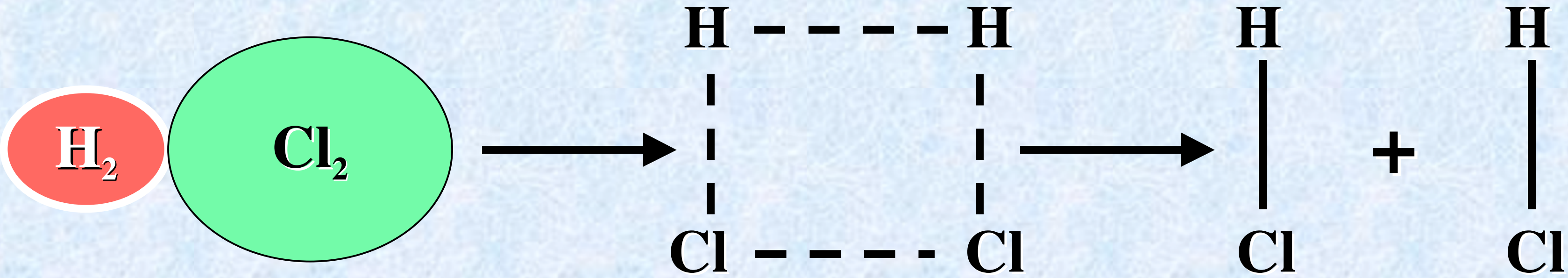
Chemical Kinetics

The Binary Collision Model

Must actually have a hydrogen molecule bump into a chlorine molecule to have chemistry occur. Reaction during such a collision might look like the following picture:

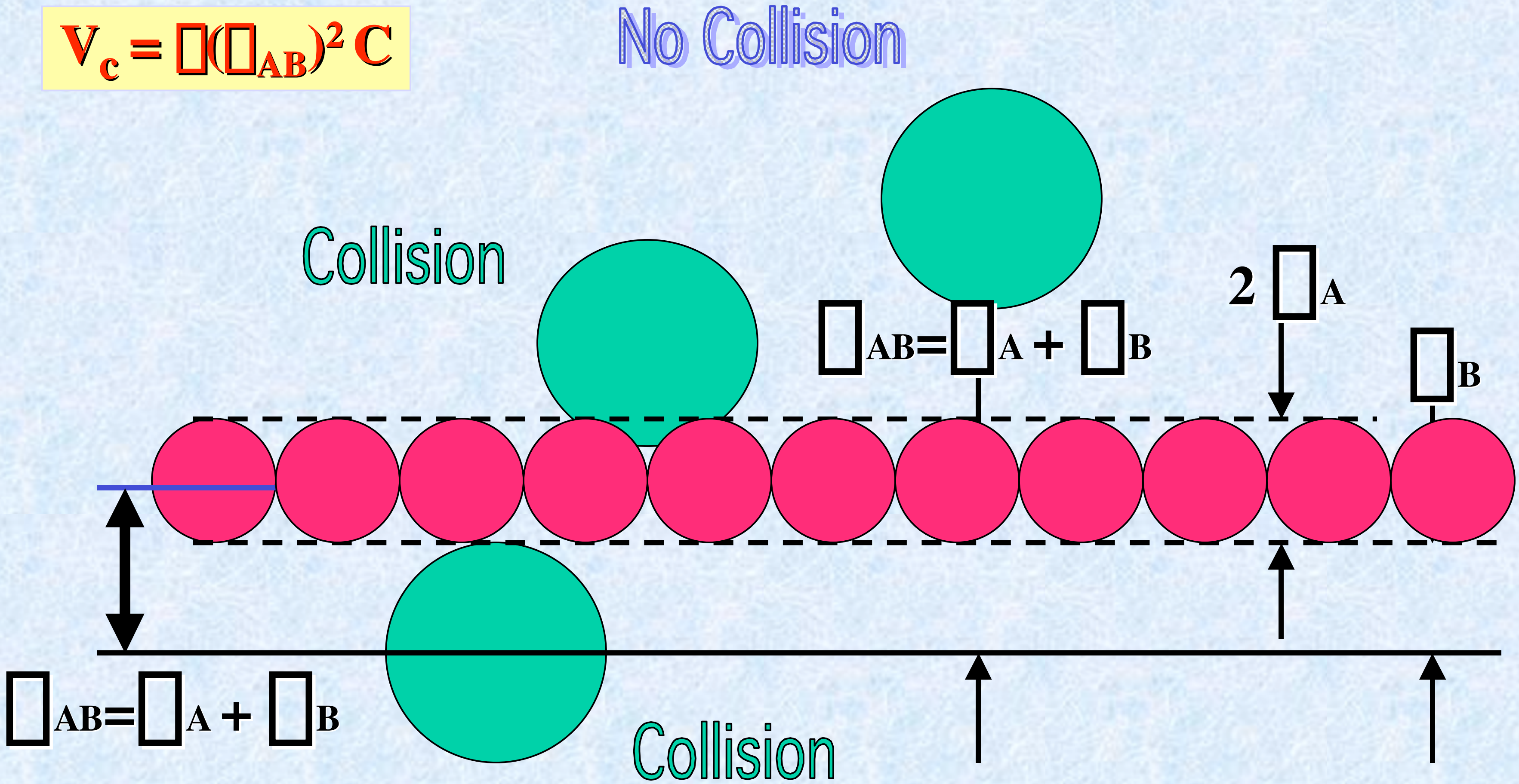

H2
Cl2
H
H
Cl
Cl
H
Cl
+
H
Cl

Collision Frequency

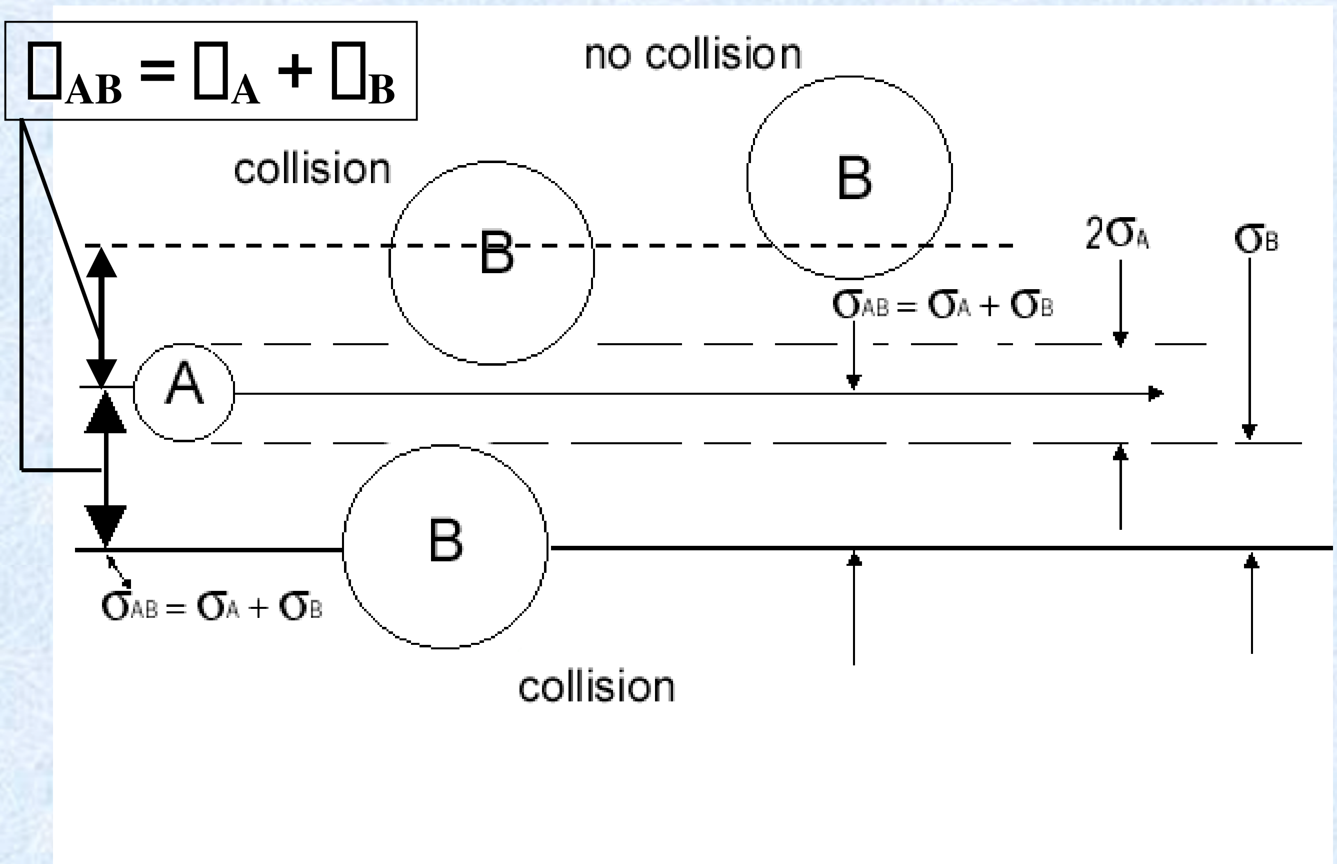
Real gases consist of particles of finite size that bump into each other at some finite rate.

Assume first that the red molecule has a constant speed C and the green ones are standing still.

$V_c = □(□_{AB})^2 C$



If a green molecule has some piece in this volume□ Collision!



σ_A is the radius of molecule A, σ_B the radius of B

There is one subtlety. In deriving z, we assumed the red molecule flew through a cloud of motionless green ones at a speed of C.

In reality, of course, all the molecules are moving.

$\langle u_{rel} \rangle$ is the mean speed of molecule A with respect to molecule B.

Where $\mu = m_A\, m_B/(m_A + m_B)$

μ is called the reduced mass and can be thought of as a kind of (geometric) average of the masses of A,B.

Bonus * Bonus * Bonus * Bonus * Bonus * Bonus

$zN_A = \pi(\sigma_{AB})^2 \langle u_{rel} \rangle (N_B/V) N_A$

By convention, because we don't want our results to depend on the size or volume V of our experimental apparatus, we define Z_{AB}:

Z_{AB} is the total number of collisions between all A and all B Molecules per liter (or per ml depending on units used for V).

Note that Z_{AB} depends on 4 things:

A Subtlety that arises when A=B

When we multiply z by N_A we count the collisions of all A molecules with all B molecules. When A=B (all collisions are of A with other A's) this turns out to count all collisions twice!

Thus, $\langle u_{rel} \rangle = (2)^{1/2}(8kT/\pi m_A)^{1/2}$

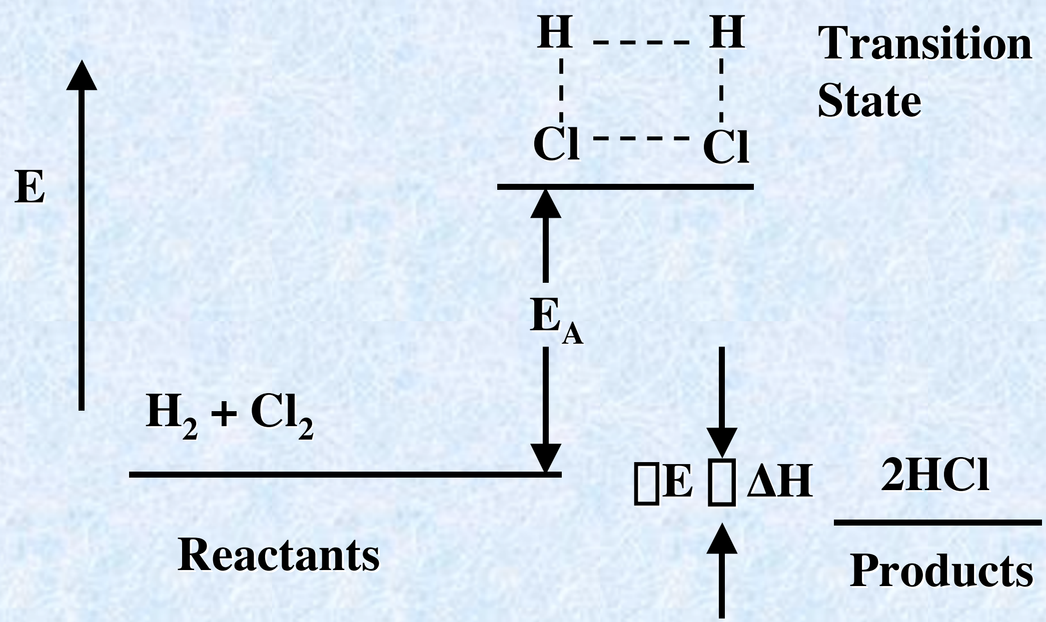
$(8kT/\pi m_A)^{1/2}$ is the average speed of a molecule even as $(3kT/m_A)^{1/2}$ is the root mean square speed of a molecule

This gives:

$$Z_{AA} = (1/2)\,(2)^{1/2}\,\pi(\sigma_{AA})^2\,(8kT/\pi m_A)^{1/2}\,(N_A/V)^2$$

Bonus * Bonus * Bonus * Bonus * Bonus * Bonus

Reaction Energy Barriers



As a result, we are not interested in the total collision rate Z_{AB}, but rather how much energy is available in the collision which in turn depends on the relative speed of A,B approach.

Even knowing how Z depends on energy is not sufficient. We must also know the probability of reaction at a given energy.

A very simple model for P_R is the "all or nothing" model where $P_R(E)=0$, $E<E_A$ and $P_R(E)=1$, $E \geq E_A$.

By convention P_R is associated with the collision "cross section" $(\square_{AB})^2$:

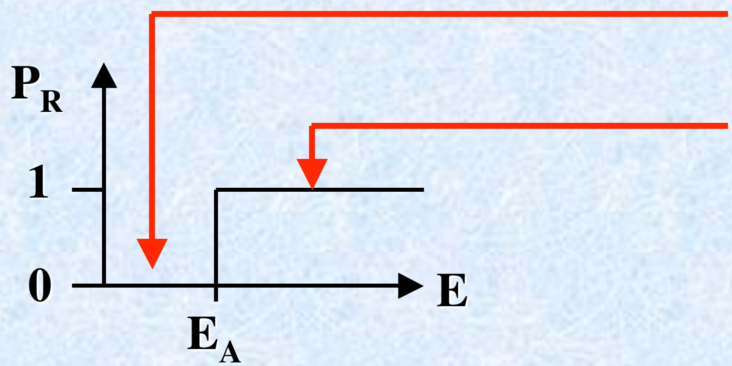
The reaction cross section, $(\square_R)^2$, is the product of the reaction probability, P_R, at a given energy and the collision cross section, $(\square_{AB})^2$.

Reaction “Cross Section” $\square_R{}^2$

A + B □ Products

All or Nothing Model

$\square_R{}^2 = P_R \square_{AB}{}^2$



□

$P_R(E) = 0$ when $E \leq E_A$

$P_R(E) = (1 - E_A/E)$ when $E > E_A$

Reaction Cross Section

A+B → Product

Arrhenius Model

$\square_R^2 = P_R \, \square_{AB}^2$