Simple Collision Theory

1. The Arrhenius Equation

$$k = A e^{-E_A/RT} \qquad (1)$$

2. Collision Theory

From the kinetic theory of gases the collision number, Z_{AB}, which describes the number of collisions per volume per second is given by

$$Z_{AB} = [A][B] (r_A + r_B)^2 \left(\frac{8\pi kT}{\mu}\right)^{\frac{1}{2}} = Z'[A][B] \qquad (2)$$

where $\mu = \frac{m_A m_B}{m_A + m_B}$ and is the reduced mass.

For typical gas phase reaction partners the relative molecular or atomic masses will be about 40 so that $\mu \sim 20$, $r_A + r_B \sim 0.3$ nm. This gives at 300 K the following values of Z' :-

$$Z' \sim 10^{11}\ dm^3\ mol^{-1}\ s^{-1}$$

or $\sim 2 \times 10^{-10}\ cm^3\ molecules^{-1}\ s^{-1}$.

The rate of reaction is given by the fraction of collisions with energy along the line of centres greater than E_C, so

$$\text{rate} = Z_{AB}\, e^{-E_C/RT} = k[A][B] \qquad (3)$$

Substitution of (1) and (2) in (3) gives

$$E_A = E_C$$

and $A = Z'$.

We find that for most gas reactions

$$A < Z'$$

and so we write

$$k = P\, Z'\, e^{-E_A/RT}$$

where $P = A/Z'$.

Some P Factors

Gas Reactions	Value of p.
$NO_2 + CO \longrightarrow NO + CO_2$	$^1/_3$
$NO_2 + O_3 \longrightarrow NO_3 + O_2$	10^{-1}
$NO + O_3 \longrightarrow NO_2 + O_2$	10^{-2}
$NO + C\ell_2 \longrightarrow NOC\ell + C\ell$	4×10^{-3}
$F_2 + C\ell O_2 \longrightarrow FC\ell O_2 + F$	10^{-3}

Two Solution Reactions

$[Co\ (NH_3)_5\ Br]^{2+} + Hg^{2+} \longrightarrow$ $[Co\ (NH_3)_5\ H_2O]^{3+}\ Hg\ Br^+$	3×10^{-6}
$[Co\ (NH_3)_5\ Br]^{2+} + OH^- \longrightarrow$ $[Co\ (NH_3)_5\ OH]^{2+} + Br^-$	10^{+4}