

Simple Collision Theory

1. The Arrhenius Equation

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

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

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

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' :-

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

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

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

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

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

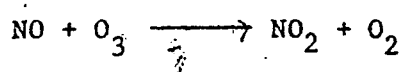
Value of p.



$$1/3$$



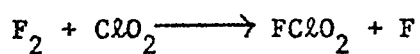
$$10^{-1}$$



$$10^{-2}$$

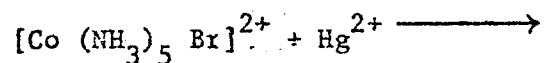


$$4 \times 10^{-3}$$

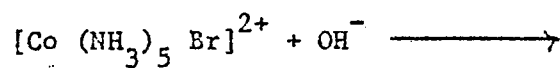
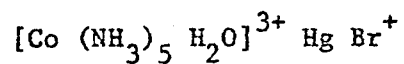


$$10^{-3}$$

Two Solution Reactions



$$3 \times 10^{-6}$$



$$10^{+4}$$

