Chemical Kinetics

Note Title 2/2/2010

Understanding rate expressions:

$$A + B \rightarrow C + D$$

bimolecular reaction
i.e. two reactants

$$\frac{d[C]}{dt} = \frac{d[D]}{dt} = k[A][B]$$

$[X] \rightarrow$ concentration of X (cg molecules / cm^3)

$k \rightarrow$ rate constant (cg cm^3 / (molecule sec))

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k[A][B]$$

Eg of bimolecular reactions:

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

Self reaction (special case of bimolecular rxn)

$$A + A \rightarrow B + C$$

$$\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2 = -\frac{1}{2}\frac{d[A]}{dt}$$

note the square

note the ½ term

Three body Reactions:

$$\left.\begin{array}{l} A + B \rightarrow AB^* \\ AB^* \rightarrow A + B \\ AB^* + M \rightarrow AB + M^* \\ M^* \rightarrow M + \text{heat} \end{array}\right\} \quad A + B + M \rightarrow AB + M$$

Eg:

$$O + O_2 + M \rightarrow O_3 + M$$

$$\frac{d[O_3]}{dt} = k[O][O_2][M] \quad \text{since/if } [M] \text{ is abundant.}$$

Reverse Reactions and Chemical Equilibria:

$$A + B \xrightarrow{k_1} C + D$$

$$C + D \xrightarrow{k_2} A + B$$

$$A + B \rightleftharpoons C + D$$

$$k_1 [A][B] = k_2 [C][D]$$

$$K = \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

equilibrium constant

Photolysis:

Needs energy from photon to break chemical bond

$$X + h\nu \rightarrow Y + Z$$

$$\frac{d[Y]}{dt} = \frac{d[Z]}{dt} = k[X] = -\frac{d[X]}{dt}$$

photolysis rate constant

Eg:

highly reactive

$$O_2 + h\nu \rightarrow O + O$$

$$(\lambda < 240 \text{ nm})$$

Chain Reactions:

Initiation: non-radical + $h\nu \rightarrow$ radical + radical

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ ($\lambda < 320$ nm)

Propagation: radical + non-radical $\rightarrow$ radical + non-radical

$O(^1D) + M \rightarrow O + M$

Termination: radical + radical $\rightarrow$ non radical + non-radical

slow (since radical concs are too small)

dynamics