Lecture Notes CC: Chemical Kinetics II

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1. Elementary steps in a chemical reaction

Unimolecular reaction

A --> B or A --> B+C

example: decomposition: N_2O_5 ---> NO_2 + NO_3

isomerization:

Concentration dependence: If I have more A, then more A will fall apart

first order in [A], rate = k[A]

Bimolecular reaction

A + B --> C or A+ B --> C+D second order reaction (first order in [A] and [B])

example: NO + NO ---> N_2O_2

Concentration dependence: Need A and B to collide, so first order in [A] and [B]
second order overall
rate = k [A] [B]
it usually takes many collisions for a reaction to occur.

Termolecular reaction (rare, most single-step reactions are uni- or bi- molecular)

I (g) + I (g) + Ar --> I_2 (g) + Ar

Concentration dependence: Need all three to collide, rate = $[I]^2$ [Ar]

2. Multi-step reactions

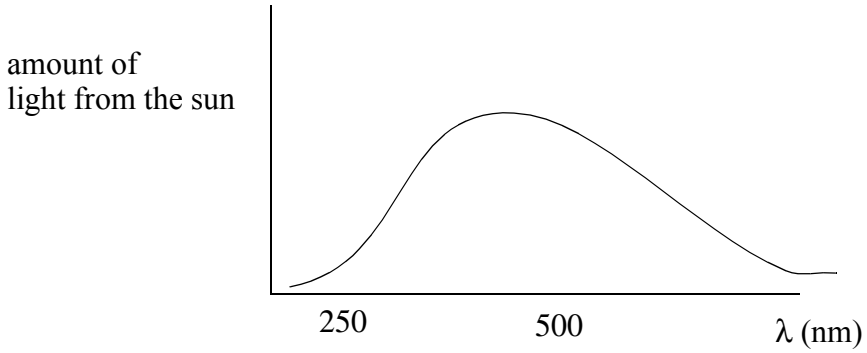
Catalytic destruction of ozone (one of many pathways):

$Cl + O_3 \text{ -- > } ClO + O_2$
$ClO + O \text{ --> } Cl + O_2$

$O_3 + O \text{ ---> } 2\ O_2$

Cl is a catalyst, because it helps the reaction along, but is neither consumed nor produced in the reaction

ClO is a reaction intermediate, because it exists only while the reaction is proceeding.



Ozone Production

Ozone blocking of UV radiation

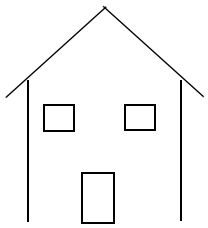
$2\ [\ Cl + O_3 \text{ --> } ClO + O_2\ ]$

$2ClO + M \text{ --> } ClOOCl + M$

$ClOOCl + hv \text{ --> } ClOO + Cl$

$ClOO + M \text{ --> } Cl + O_2 + M$

$2\ O_3 \text{ --> } 3\ O_2$



Chlorine resevoir

$Cl \text{ <--> } HCl, ClONO_2, ...$

Concept:

Consider the following biochemical reaction system:

sucrose + glycosidase ---> (sucrose-glycosidase complex)

(sucrose-glycosidase complex) ---> glycosidase + fructose + glucose

The ensyme glycosidase is: a) an intermediate b) a catalyst
the (sucrose-glycosidase complex) is: a) an intermediate b) a catalyst

3. Relation between kinetics and equilibrium

For an elementary (single-step) reaction:

$$A + B \underset{k_{reverse}}{\overset{k_{forward}}{\rightleftharpoons}} C + D$$

forward rate = $k_{forward}[A][B]$

reverse rate = $k_{reverse}[C][D]$

At equilibrium, the concentrations no longer change, so the forward and reverse rates are equal,

For a multi-step reaction:

$$Cl + O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClO + O_2 \qquad K_1 = k_1/k_{-1}$$

$$ClO + O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cl + O_2 \qquad K_2 = k_2/k_{-2}$$

$$O_3 + O \text{ ---> } 2\,O_2 \qquad K = (k_1k_2)/(k_{-1}k_{-2})$$

4. Rate Limiting Step

Example 1: First elementary step is the slow (rate-limiting) step

Decomposition of H_2O_2, catalyzed by I^-

$H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$ slow

$H_2O_2 + IO^- \xrightarrow{k_2} H_2O + O_2 + I^-$ fast

$2\ H_2O_2 \dashrightarrow 2\ H_2O + O_2$

Example 2: Rate-limiting step is not first elementary step

$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (fast equilibrium)

$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ (slow)

$2NO + H_2 \dashrightarrow N_2O + H_2O$

Derive the rate law for the following reaction mechanism:

$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ I$ fast equilibrium

$H_2 + 2\ I \xrightarrow{k_2} 2\ HI$ slow

$H_2 + I_2 \text{ ---> } 2\ HI$

Chlorine reacts with hydrogen sulfide in aqueous solution:

$Cl_2\ (aq) + H_2S\ (aq) \text{ ---> } S(s) + 2H^+\ (aq) + 2Cl^-\ (aq)$ rate = $k\ [Cl_2]\ [H_2S]$

Which of the following mechanisms is consistent with the observed reaction rate expression?

a) $Cl_2 + H_2S \rightleftharpoons H^+ + Cl^- + Cl^+ + HS^-$ (slow)

$Cl^+ + HS^- \rightleftharpoons H^+ + Cl^- + S$ (fast)

b) $H_2S \rightleftharpoons HS^- + H^+$ (fast equilibrium)

$HS^- + Cl_2 \rightleftharpoons 2\ Cl^- + S + H^+$ (slow)