14.3 Rate Laws

Concentration and Reaction Rate

It should come as no surprise that the Rate of Formation or Dissapearance is directly proportional to the concentration.

$$aA + bB = cC + dD$$

$$\text{Initial Reaction Rate} = k[A]^x[B]^y$$

x : is referred to as the order with respect to A.
y : is referred to as the order with respect to B.
$x + y$: is the overall order of the reaction.
k : is the rate constant.

Note 1: x and y are not necessarily equal to a and b. In fact x and y can only be determined experimentally.

Note 2: Our discussion will initially be confined to orders, 0, 1 and 2.

For A:
Zero Order : Initial Rate $= k[A]^0$
First Order : Initial Rate $= k[A]^1$
Second Order : Initial Rate $= k[A]^2$

14.3 Rate Laws

Determining Rate Law Using the Method of Initial Rates

$NO + O_3 = NO_2 + O_2$

a) What is the rate law?

b) What is the rate constant?

Exp	$[NO]_o$, M	$[O_3]_o$, M	Initial Rate, Ms^{-1}
1	0.139	0.0436	0.527
2	0.139	0.0872	1.05
3	0.278	0.0436	1.05
4	0.278	0.0872	2.11

Exp 1: $Rate_1 = k[NO]_1^x [O_3]_1^y$

$0.527 = k(0.139)^x(0.0436)^y$

Exp 2: $Rate_2 = k[NO]_2^x [O_3]_2^y$

$1.05 = k(0.139)^x(0.0872)^y$

$$\frac{Rate_2}{Rate_1}: \frac{1.05}{0.527} = \frac{k(0.139)^x(0.0872)^y}{k(0.139)^x(0.0436)^y}$$

$1.99 = 2^y$

$y = 1$

Exp 1: $0.527 = k(0.139)^x(0.0436)^y$

Exp 3: $Rate_3 = k[NO]_3^x [O_3]_3^y$

$1.05 = k(0.278)^x(0.0436)^y$

$$\frac{Rate_3}{Rate_1}: \frac{1.05}{0.527} = \frac{k(0.278)^x(0.0436)^y}{k(0.139)^x(0.0436)^y}$$

$1.99 = 2^x$

$x = 1$

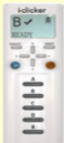
Initial Rate $= k[NO][O_3]$

Exp 1: $0.527 = k(0.139)(0.0436)$

$$k = \frac{0.527}{(0.139)(0.0436)} = 86.9\ M^{-1}s^{-1}$$

14.3 Rate Laws

Determining Rate Law Using the Method of Initial Rates



$2\ ICl + H_2 = I_2 + 2\ HCl$

a) What is the overall order of the reaction? 3

Exp	$[ICl]_o$, M	$[H_2]_o$, M	Initial Rate, Ms^{-1}
1	0.309	0.114	7.07e-3
2	0.618	0.114	1.41e-2
3	0.309	0.228	2.83e-2
4	0.618	0.228	5.65e-2

Previously we did this the long way, this time we will short cut it!

Initial Rate $= k[ICl]^x [H_2]^y$

Exp 1 & 3: [ICl] is held constant while the $[H_2]$ increases by a factor of 2

$$\frac{3}{1} : \frac{2.83 \times 10^{-2}}{7.07 \times 10^{-3}} = 4$$

$$2^y = 4$$

$$y = 2$$

Exp 1 & 2: $[H_2]$ is held constant while the [ICl] increases by a factor of 2.

$$\frac{2}{1} : \frac{1.41 \times 10^{-2}}{7.07 \times 10^{-3}} = 2$$

$$2^x = 2$$

$$x = 1$$

Overall Order $= x + y$

$= 1 + 2$

$= 3$

14.4 Concentration Changes over Time

Integrated Rate Laws

Integrated Rate Laws for Reactions of Type A → Products

Reaction Order	Rate Law	Integrated Rate Law
Zero order	rate = $k\,[A]^0 = k$	$[A]_t = [A]_0 - kt$
First order *	rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$
Second order	rate = $k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$

t : time.
$[A]_0$: initial concentration at $t = 0$.
$[A]_t$: concentration at $t = t$.

A = Products

$$-\frac{\Delta[A]}{\Delta t} = k[A]$$

$$\frac{d[A]}{dt} = -k[A] \quad \text{... if } \Delta \text{ is very small}$$

$$\left(\frac{1}{[A]}\right) d[A] = -k\,dt$$

$$\int_{t=0}^{t=t} (1/[A])\, d[A] = -k \int_{t=0}^{t=t} dt$$

$$\ln [A]_t - \ln [A]_0 = -kt$$

$$\boxed{\ln \frac{[A]_t}{[A]_0} = -kt}$$