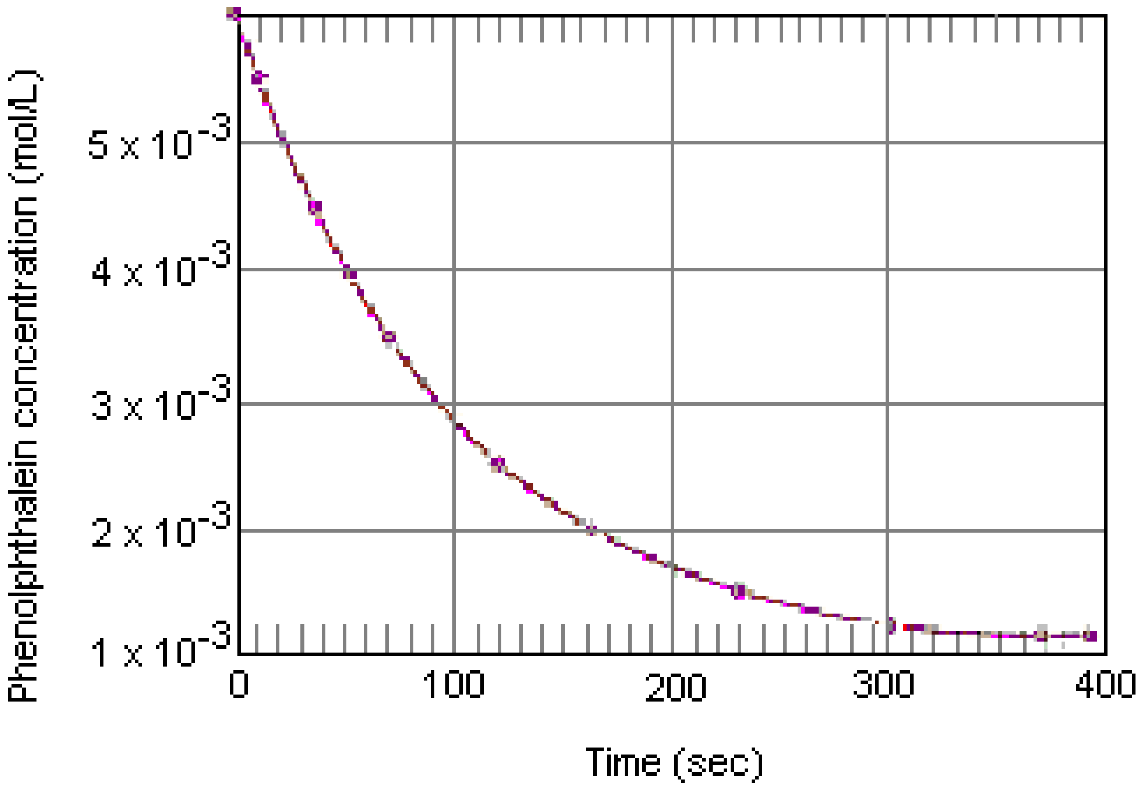
Chemical Kinetics

Nikhila Tippannawar
Chemistry Dept.
Arihant College of Arts,
Commerce and Science

Phenolphthalein reacting with OH^- ion



Rate of reaction = $\Delta X / \Delta t$

X = Concentration of Phenolphthalein (M)	Time (s)
0.0050	0.0
0.0045	10.5
0.0040	22.3
0.0035	35.7
0.0030	51.1
0.0025	69.3
0.0020	91.6
0.0015	120.4
0.0010	160.9
0.00050	230.3
0.00025	299.6
0.00015	350.7
0.00010	391.2

M = moles/liter

Problem 1

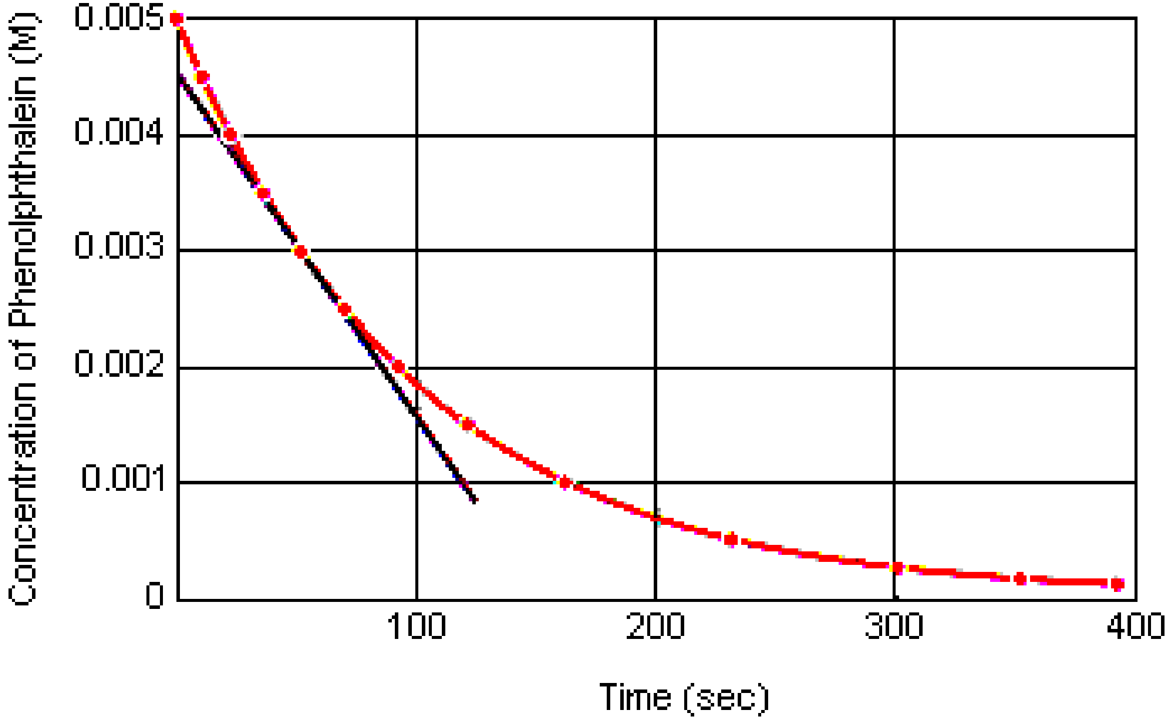
Use the data in the above table to calculate the rate at which phenolphthalein reacts with the OH^- ion during each of the following periods:

(a) During the first time interval, when the phenolphthalein concentration falls from 0.0050 M to 0.0045 M.

(b) During the second interval, when the concentration falls from 0.0045 M to 0.0040 M.

(c) During the third interval, when the concentration falls from 0.0040 M to 0.0035 M.

Reaction rate varies with time.
Instantaneous rate of reaction = dX/dt
= the rate at each instant



Rate = k $X_{phenolphthalein}$.

Problem 2

Calculate the rate constant for the reaction between phenolphthalein and the OH- ion if the instantaneous rate of reaction is 2.5 x 10^{-5} mole per liter per second when the concentration of phenolphthalein is 0.0025 M.

$$\frac{2.5 \times 10^{-5}\ \mathrm{mol/L}}{1\ \mathrm{s}} = k(0.0025\ \mathrm{mol/L})$$

$k = 0.010\ s^{-1}$.

Expressing the rate of reaction

$$2\ HI = H_2(g) + I_2(g)$$

k = rate constant for forming H_2 or I_2

k' = rate constant for destroying HI

Problem 4. Calculate the rate at which HI disappears at the moment when I_2 is being formed at a rate of 1.8×10^{-6} moles per liter per second.

Hint: HI disappears twice as fast as I_2 is formed!

Can you figure out the rate of a reaction from its stoichiometry alone?

$$CH_3Br + OH^- \Leftrightarrow CH_3OH + Br^-$$

Experiments showed that

$$\text{Rate} = k\,(CH_3Br)\,(OH^-)$$

A very simlar reaction:

$(CH_3)_3CBr + OH^- <=> (CH_3)_3COH + Br^-$

One might expect a rate = $k [(CH_3)_3CBr] [OH^-]$

Rate = $k [(CH_3)_3CBr]$

The rate law for a reaction must be determined experimentally!

Why????? Why can't chemistry be easy????

Some reactions occur in a single step.
Some don't!!

The rate of reaction will be determined by the slowest intermediate step.

"Rate-determining" step

"Rate-limiting" step

Example: Decomposition of N_2O_5 into NO_2 and O_2 .

Step 1: $N_2O_5 <=> NO_2 + NO_3$ unimolecular

Step 2: $NO_2 + NO_3 <=> NO_2 + NO + O_2$ bimolecular

Step 3: $NO + NO_3 <=> 2\ NO_2$ bimolecular

molecularity

$N_2O_5 <=> NO_2 + NO_3$

First order — Rate depends on (N_2O_5)

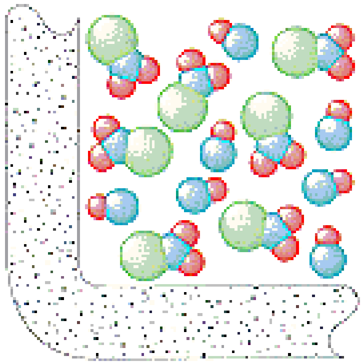
Decomposition of HI

second order — Rate depends on $(HI)^2$.

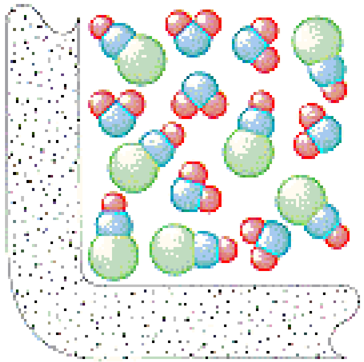
What is the order of $2\ NO + O_2 <=> 2\ NO_2$?

Collision theory model of chemical reactions

The rate of any step in a reaction is proportional to the concentrations of the reagents consumed in that step.



The rate law for a one-step reaction should therefore agree with the stoichiometry of the reaction.



Summary

The rate laws for chemical reactions can be explained by the following general rules.

1. The rate of any step in a reaction is directly proportional to the concentrations of the reagents consumed in that step.
2. The overall rate law for a reaction is determined by the sequence of steps, or the mechanism, by which the reactants are converted into the products of the reaction.
3. The overall rate law for a reaction is dominated by the rate law for the slowest step in the reaction.