Reaction rates - Chemical Kinetics

The study of reaction rate is called chemical kinetics.

Reaction Rate

Rate indicates how fast something changes with time. Rate describe change over time. It is the speed of the reaction.

Reaction rate is the rate at which a chemical reaction takes place. it is measured by the rate of the formation of the product or the rate of the disappearance of the reactants.

Rate = - [change in the concentration of the reactant]/ change of time

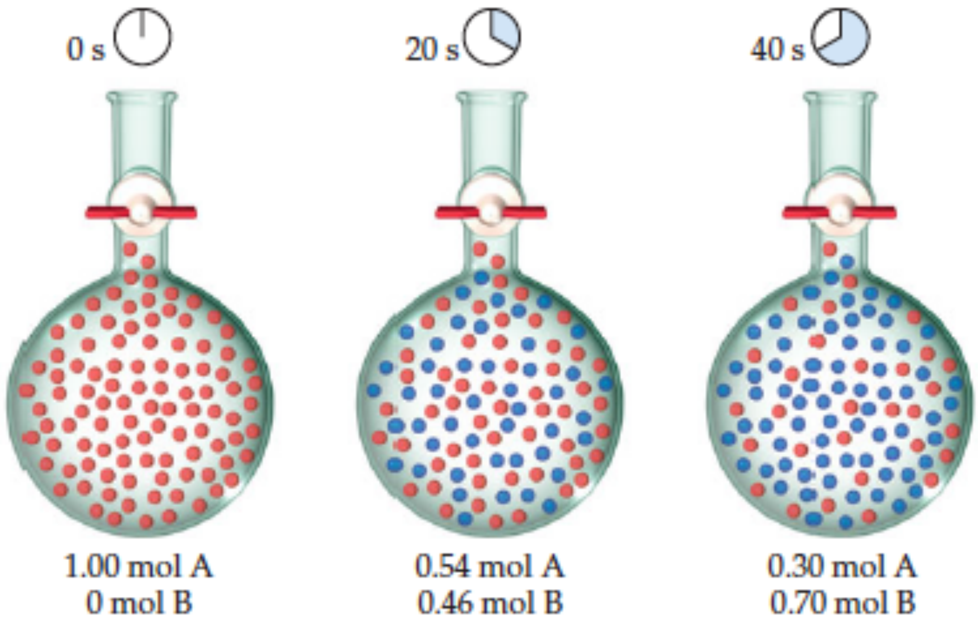
= [change in the concentration of the product/ change of time

$$\text{Rate} = -\Delta\,[\text{reactant}] / \Delta T$$

$$= \Delta\,[\text{product}] / \Delta T$$

The sign is negative because the rate during a reaction must be a positive number.
The concentrations of the products are all increasing, so the sign of their rate expressions are positive.

Example: **A ---> B**



Rate of appearance of B:

$$\text{Average rate} = \frac{0.46\ M - 0.00\ M}{20\ \text{s} - 0\ \text{s}} = 2.3 \times 10^{-2}\ M/\text{s}$$

Rate of disappearance of A:

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.54\ M - 1.00\ M}{20\ \text{s} - 0\ \text{s}} = 2.3 \times 10^{-2}\ M/\text{s}$$

Example:

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$$

$$\text{rate} = \frac{-\Delta[CH_3OCH_3]}{\Delta t} = \frac{\Delta[CH_4]}{\Delta t} = \frac{\Delta[CO]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t}$$

Balanced coefficient appear in the rate definition.

consider the following reaction:

$$2N_2O_5(s) \longrightarrow 4NO_2(g) + O_2(g)$$

In order to define the reaction rate, we divide by the coefficients from the balanced equation.

$$\text{rate} = \frac{-\Delta[N_2O_5]}{2\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

The rate decreases gradually as the reaction proceeds. The rate becomes zero when the reaction is complete.

Reaction rate can be measured.

To measure a reaction rate, you need to be able to keep track of how the concentration of the one or more reactants or products changes over time.

Example: Decomposition of dinitrogen pentaoxide:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Table 1 Concentration Data and Calculations for the Decomposition of N_2O_5

t (s)	$[NO_2]$ (M)	$\Delta[NO_2]$ (M)	Δt (s)	$\Delta[NO_2]/\Delta t$ (M/s)	Rate (M/s)
0	0	4.68×10^{-3}	20.0	2.34×10^{-4}	5.85×10^{-5}
20.0	0.00468	4.22×10^{-3}	20.0	2.11×10^{-4}	5.28×10^{-5}
40.0	0.00890	3.82×10^{-3}	20.0	1.91×10^{-4}	4.78×10^{-5}
60.0	0.01272	3.44×10^{-3}	20.0	1.72×10^{-4}	4.30×10^{-5}
80.0	0.01616				

Concentration must be measured often in a small time interval.

The reaction rate decreases with time.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

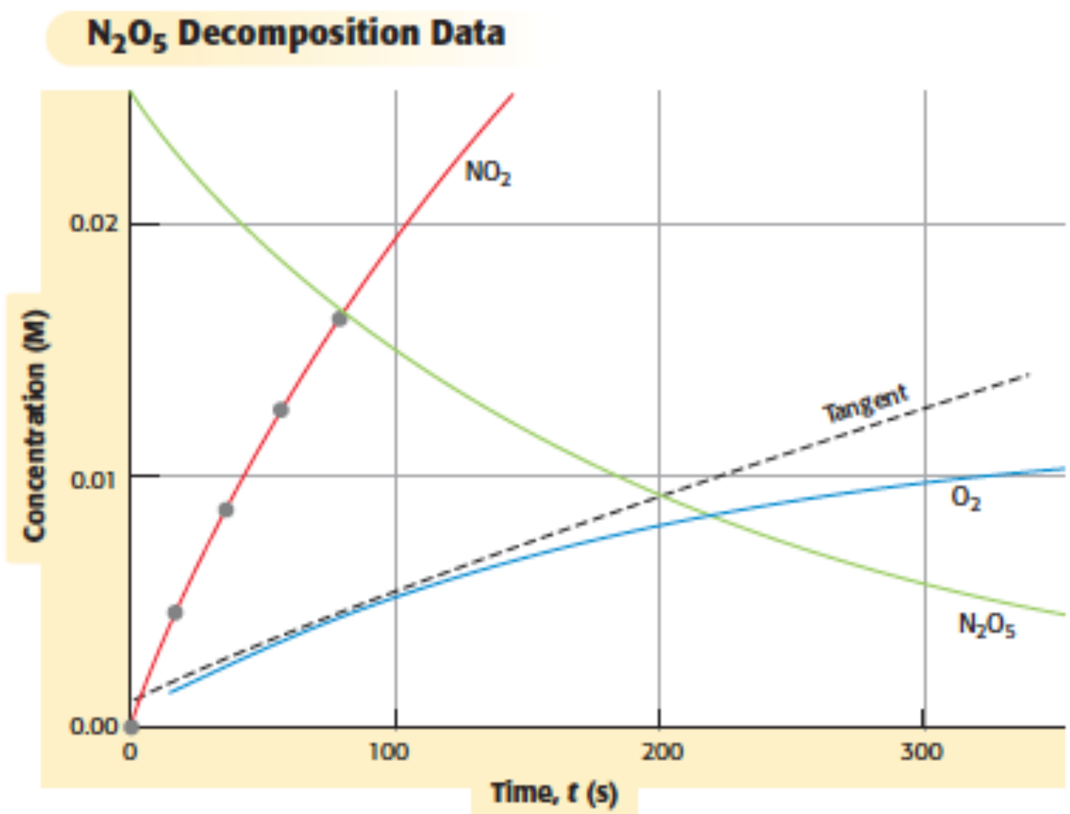
$$\text{rate} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{0.01616\ \text{M} - 0.01272\ \text{M}}{4(80.0\ \text{s} - 60.0\ \text{s})} = 4.30 \times 10^{-5}\ \text{M/s}$$

This result shows the rate of the reaction after it has been going on for about 70 s.

Reaction rate can be represented graphically.

Graph shows how the concentrations of the reactants and products change with time.

The graph shows the changes in the concentration with time during the decomposition of nitrogen pentoxide. The points represent the data used in table 1 (above).



Notice that the graph shows that the concentration of nitrogen dioxide increases four times faster than the concentration of the oxygen increases. The result agrees with the 4:1 ratio of nitrogen dioxide to oxygen in the balanced equation.

The slope of the three curves measures the rates of change of each concentration.

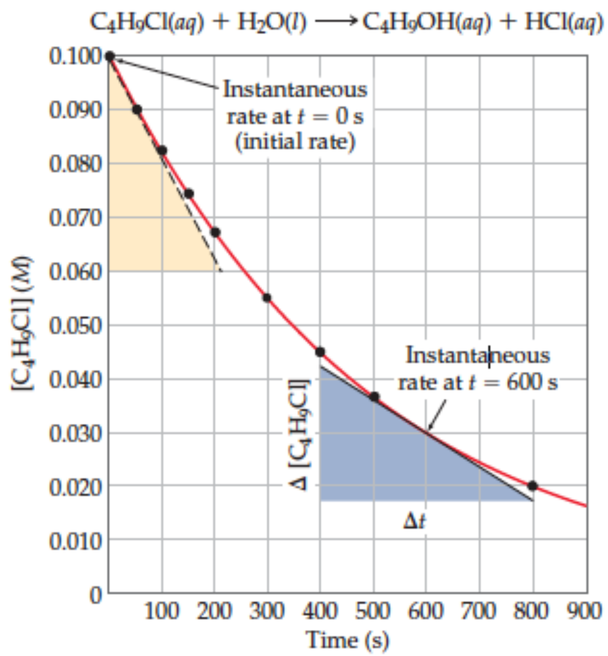
Oxygen is a product and its coefficient in the equation is 1. The slope of the O_2 curve is simply the reaction rate.

$$\text{slope of } O_2 \text{ curve} = \frac{\Delta[O_2]}{\Delta t} = \text{rate of the reaction}$$

A line has been drawn as a tangent to the O_2 curve at t = 70 s. Slope = rise/run = 4.30×10^{-5} M/s. This value agrees with the rate calculated in Table 1 at the same instant.

The rate of the same reaction is the slope of $NO_2/4$, because the coefficient of NO_2 is 4.

Example:



The instantaneous rate at $t = 600$ s is:

$$\text{Instantaneous rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.017 - 0.042)\,M}{(800 - 400)\text{s}}$$
$$= 6.3 \times 10^{-5}\,M/\text{s}$$

The instantaneous rate at $t = 0$ s is:

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100)\,M}{(210 - 0)\text{ s}} = 1.9 \times 10^{-4}\,M/\text{s}$$

Example:

$$2Br^-(aq) + H_2O_2(aq) + 2H_3O^+(aq) \longrightarrow Br_2(aq) + 4H_2O(l)$$

Time t (s)	$[H_3O^+]$ (M)	$[Br_2]$ (M)
0	0.0500	0
85	0.0298	0.0101
95	0.0280	0.0110
105	0.0263	0.0118

$$\Delta[H_3O^+] = (0.0263\ M) - (0.0280\ M) = -0.0017\ M$$
$$\Delta[Br_2] = (0.0118\ M) - (0.0110) = 0.0008\ M$$

From the change in hydronium ion concentration,

$$\text{rate} = \frac{-\Delta[H_3O^+]}{2\Delta t} = \frac{-(-0.0017\ M)}{2(10\ s)} = 8.5 \times 10^{-5}\ M/s$$

From the change in bromine concentration,

$$\text{rate} = \frac{\Delta[Br_2]}{\Delta t} = \frac{0.0008\ M}{10\ s} = 8 \times 10^{-5}\ M/s$$

Factors affecting rate.

Concentration, pressure, temperature and surface area are the most important factors on which the rate of a chemical reaction depends.

Concentration affects reaction rate

The reaction rate increases when the concentration of the reactants are increased.

Concentration affects noncollision reaction rates.

When the concentration increases, the number of molecules increases and the reaction rate increases.

Pressure affects the rates of the gas reactions.

Pressure has almost no effect on reactions taking place in the liquid or solid state. Doubling the pressure of a gas doublers its concentration. So, changing the pressure of a gas mixture is just another way of changing the concentration.

Temperature greatly influences the reaction rate.

All chemical reactions are affected by temperature. In almost every case, the rate of a chemical reaction increases with increasing temperature.

Temperature affects reactions everyday life. The reactions that cause food to spoil occur much more slowly when food is placed in a refrigerator or freezer.

Surface ares can be an important factor.

You get a bigger blaze with small pieces of wood, because the surface area of many small pieces is greater than that of one larger piece of wood.