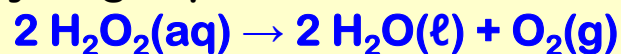


14.2 Expressing the Rate of a Reaction

Average Rate and Reaction Stoichiometry

For the decomposition of hydrogen peroxide in dilute sodium hydroxide at 20 °C,



the **average rate of disappearance** of H_2O_2 over the period from $t = 0$ to $t = 516$ min is found to be $8.08 \times 10^{-5} \text{ M/min}$.

What is the **average rate of appearance** of O_2 over the same period?

What is the **average rate of the reaction**?

$$\text{Average Rate of Reaction} = -\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = \frac{1}{1} \frac{\Delta[\text{O}_2]}{\Delta t}$$

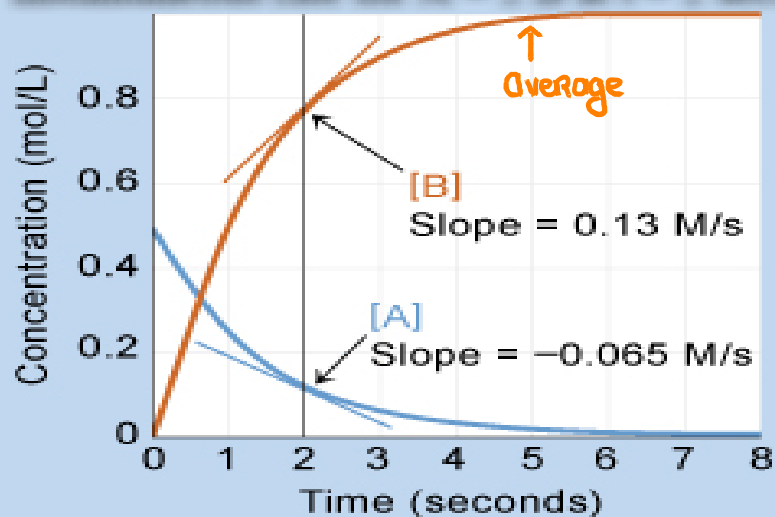
$$-\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = 8.08 \times 10^{-5} \text{ M} \cdot \text{min}^{-1}$$

$$\begin{aligned} \frac{\Delta[\text{O}_2]}{\Delta t} &= -\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} \\ &= \frac{1}{2} \left(-\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} \right) \\ &= \frac{1}{2} (8.08 \times 10^{-5} \text{ M} \cdot \text{min}^{-1}) \\ &= 4.04 \times 10^{-5} \text{ M} \cdot \text{min}^{-1} \end{aligned}$$

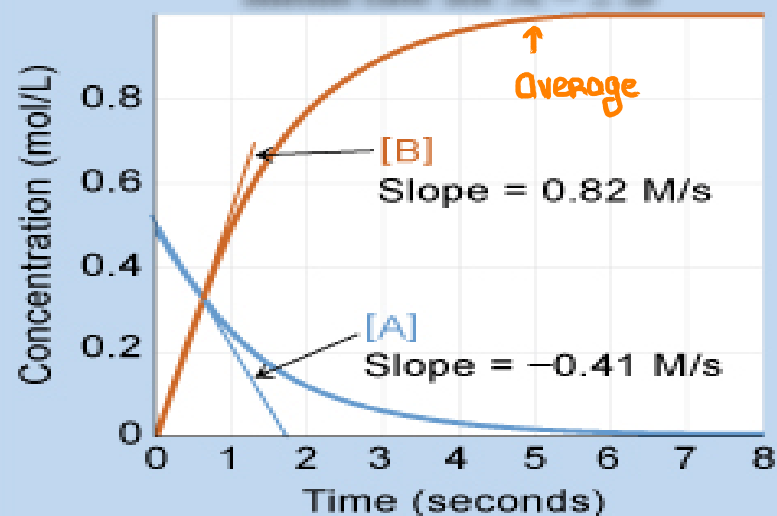
$$\begin{aligned} \text{Average Rate of Reaction} &= \frac{\Delta[\text{O}_2]}{\Delta t} \\ &= 4.04 \times 10^{-5} \text{ M} \cdot \text{min}^{-1} \end{aligned}$$

14.2 Expressing the Rate of a Reaction Instantaneous and Initial Rates

Instantaneous rate for $A = 2 B$ at $t = 2$ seconds



Initial rate for $A = 2 B$

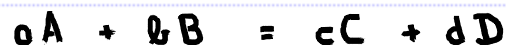


Initial Rate: Is where the Rate of Formation and the Rate of Disappearance is linear and thus becomes our region of choice.

14.3 Rate Laws

Concentration and Reaction Rate

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



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

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.

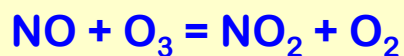
For A:

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

Exp	[NO] ₀ , M	[O ₃] ₀ , 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



- a) What is the rate law?
b) What is the rate constant?

$$\text{Exp 1: } \text{Rate}_1 = k [\text{NO}]_1^x [\text{O}_3]_1^y \\ 0.527 = k (0.139)^x (0.0436)^y$$

$$\text{Exp 2: } \text{Rate}_2 = k [\text{NO}]_2^x [\text{O}_3]_2^y \\ 1.05 = k (0.139)^x (0.0872)^y$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} : \frac{1.05}{0.527} = \frac{k (0.139)^x (0.0872)^y}{k (0.139)^x (0.0436)^y}$$

$$1.99 = 2^y$$

$$y = 1$$

$$\text{Exp 1: } 0.527 = k (0.139)^x (0.0436)^y$$

$$\text{Exp 3: } \text{Rate}_3 = k [\text{NO}]_3^x [\text{O}_3]_3^y \\ 1.05 = k (0.278)^x (0.0436)^y$$

$$\frac{\text{Rate}_3}{\text{Rate}_1} : \frac{1.05}{0.527} = \frac{k (0.278)^x (0.0436)^y}{k (0.139)^x (0.0436)^y}$$

$$1.99 = 2^x$$

$$x = 1$$

$$\text{Initial Rate} = k [\text{NO}] [\text{O}_3]$$

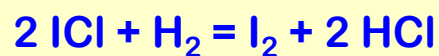
$$\text{Exp 1: } 0.527 = k (0.139)(0.0436)$$

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

14.3

Rate Laws

Determining Rate Law Using the Method of Initial Rates



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

Exp	$[\text{ICl}]_0, \text{ M}$	$[\text{H}_2]_0, \text{ M}$	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!

$$\text{Initial Rate} = k [\text{ICl}]^x [\text{H}_2]^y$$

Exp 1 & 3 : $[\text{ICl}]$ is held constant while the $[\text{H}_2]$ 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 : $[\text{H}_2]$ is held constant while the $[\text{ICl}]$ increases by a factor of 2.

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

$$2^x = 2$$

$$x = 1$$

$$\text{Overall Order} = x + y$$

$$= 1 + 2$$

$$= 3$$

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

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

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

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

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

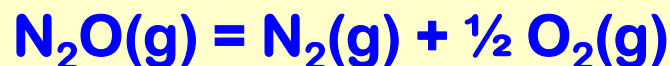
$$\ln [A]_t - \ln [A]_0 = -kt$$

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

14.4 Concentration Changes over Time

Integrated Rate Laws

The decomposition of nitrous oxide



is **second order in N_2O** with a rate constant of **$1.20 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$** .

If the initial concentration of **N_2O** is **1.79 M** , the concentration of **N_2O** will be **0.187 M** after how many **seconds**.



~?,000 s

$$\frac{1}{[\text{A}]_t} = \frac{1}{[\text{A}]_0} + kt$$

$$[\text{A}]_0 = 1.79 \text{ M}$$

$$[\text{A}]_t = 0.187 \text{ M}$$

$$k = 1.20 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$$

$$t = ?$$

$$\frac{1}{0.187} = \frac{1}{1.79} + 1.20 \times 10^{-3} t$$

$$5.348 = 0.5587 + 1.20 \times 10^{-3} t$$

$$1.20 \times 10^{-3} t = 5.348 - 0.5587$$

$$t = \frac{4.7893}{1.20 \times 10^{-3}} = 3,991 \text{ s}$$

14.4 Concentration Changes over Time

Graphical Determination of Reaction Order

Determining the Rate Equation: Graphical Method

Description

The rate law for reactions involving a single reactant can be determined using the graphical method. This method involves constructing a series of plots of concentration vs. time data and analyzing the plots to extract the reaction order and the rate constant.

The general reaction used for this tutor is:

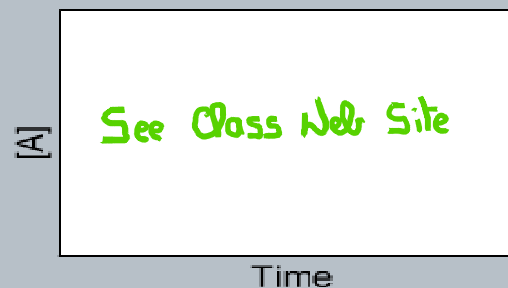


The concentration vs. time data at right were collected by running the reaction at a constant temperature. These are data taken for a single trial of the reaction.

Rate = [A]

Submit

time, min	[A], mol/L	time, min	[A], mol/L
0	0.7245	5	0.4046
1	0.6605	6	0.3406
2	0.5965	7	0.2766
3	0.5325	8	0.2126
4	0.4686		



- [A] vs. Time
- ln[A] vs. Time
- 1/[A] vs. Time
- Least Squares

Plot