

# Rate Law

Each reaction has its own equation which gives its rate as a function of \_\_\_\_\_  
\_\_\_\_\_. This is called the “\_\_\_\_\_”.

Rate laws \_\_\_\_\_ be determined experimentally. They can't be deduced from the equation alone. To determine rate law, we will measure the rate at different starting concentrations.



Experiment Number	Initial $NH_4^+$ Concentration (M)	Initial $NO_2^-$ Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	$5.4 \times 10^{-7}$
2	0.0200	0.200	$10.8 \times 10^{-7}$
3	0.0400	0.200	$21.5 \times 10^{-7}$
4	0.0600	0.200	$32.3 \times 10^{-7}$
5	0.200	0.0202	$10.8 \times 10^{-7}$
6	0.200	0.0404	$21.6 \times 10^{-7}$
7	0.200	0.0606	$32.4 \times 10^{-7}$
8	0.200	0.0808	$43.3 \times 10^{-7}$

Compare Experiment number 1 and 2. What do you notice?

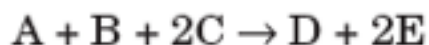
Compare Experiment number 5 and 6. What do you notice?

Exponents tell the **order** of the reaction with respect to each reactant. This reaction is **First-order** in  $[\text{NH}_4^+]$ , **First-order** in  $[\text{NO}_2^-]$ . The **overall reaction order** can be found by adding the exponents on the reactants in the rate law. This reaction is **second-order overall**.

The general rate expression:

$k$  is \_\_\_\_\_ for each reaction, and varies with \_\_\_\_\_. A large  $k$  indicates a \_\_\_\_\_ reaction, while a small  $k$  indicates a \_\_\_\_\_ reaction.

Let's try another example. Find the rate expression from the following data:



Experiment	Initial [A] ( $\text{mol dm}^{-3}$ )	Initial [B] ( $\text{mol dm}^{-3}$ )	Initial [C] ( $\text{mol dm}^{-3}$ )	Initial rate of production of D ( $\text{mol dm}^{-3} \text{s}^{-1}$ )
1	0.05000	0.05000	0.05000	$3.125 \times 10^{-6}$
2	0.1000	0.05000	0.05000	$6.250 \times 10^{-6}$
3	0.05000	0.1000	0.05000	$1.250 \times 10^{-5}$
4	0.05000	0.05000	0.1000	$3.125 \times 10^{-6}$

Start with A. (Hint, look at 1,2)

Next, B. (Hint, look at 1,3)

Lastly, C. (Hint, 1,4)

## Units of Rate Constants

Depending on the rate of reaction with respect to the various reactants, rate expressions may be made up of varying combinations of concentration terms. It is important that the units of the rate of reaction are always  $\text{mol dm}^{-3} \text{s}^{-1}$ , so to maintain this the units of the rate constant,  $k$ , will vary from reaction to reaction.

Find the units for  $k$  if the rate expression is  $\text{Rate} = k [A]$

Find the units for  $k$  if the rate expression is  $\text{Rate} = k [A]^2$

- State the order of reaction with respect to a reactant, R, if:
  - the rate of reaction doubles when [R] doubles
  - the rate of reaction is unchanged when [R] triples
  - the rate of reaction reduces by a factor of four when [R] is halved.
- Calculate the average rate of production of carbon dioxide in  $\text{mol dm}^{-3} \text{s}^{-1}$  if 0.480 g of carbon dioxide is produced in a  $2.00 \text{ dm}^3$  flask in 1.06 minutes, according to the reaction:
 
$$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$$
- The rate expression for the reaction
 
$$5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
 is  $\text{Rate} = k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$   
 Assuming that all variables except concentration are kept constant, predict the effect on the rate of reaction if:
  - $[\text{Br}^-]$  doubles (other reactant concentrations unchanged)
  - $[\text{BrO}_3^-]$  halves (other reactant concentrations unchanged)
  - $[\text{H}^+]$  triples (other reactant concentrations unchanged)
- The reaction system  $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$  was studied at  $800^\circ\text{C}$ , yielding the results listed in the table below.

Experiment	Initial $[\text{H}_2]$ ( $\text{mol dm}^{-3}$ )	Initial $[\text{NO}]$ ( $\text{mol dm}^{-3}$ )	Initial rate of reaction ( $\text{mol dm}^{-3} \text{s}^{-1}$ )
1	0.0030	0.0030	$2.25 \times 10^{-3}$
2	0.0030	0.0060	$9.00 \times 10^{-3}$
3	0.0060	0.0030	$4.50 \times 10^{-3}$

From these results, deduce:

- the order of reaction with respect to  $\text{H}_2$
- the order of reaction with respect to NO
- the rate expression
- the overall reaction order
- the value of the rate constant, with units.