

# Rate Law



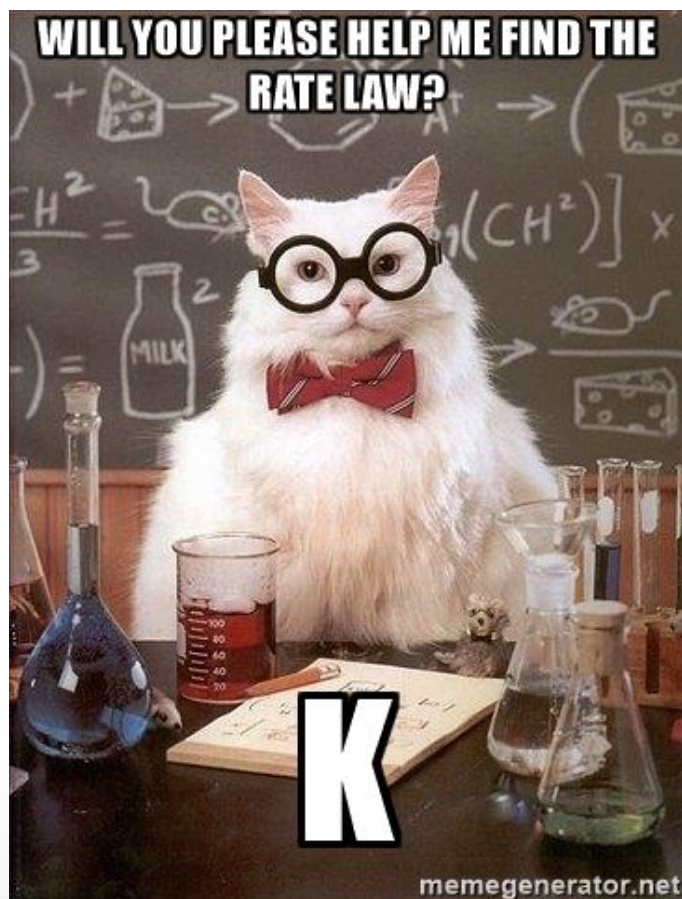
<https://www.pinterest.com/pin/442267625876101351/>

## Outcomes:

- Determine the rate law of a chemical reaction from experimental data.

# Rate Law:

- An **EXPRESSION** which relates the **RATE** of a reaction to the **CONCENTRATION** of the reactants.
- Allows us to **CALCULATE** the **RATE** of a reaction with given **CONCENTRATIONS** of **REACTANTS**.
- Shows the **QUANTITATIVE** effect of **CONCENTRATION** on reaction rate.



# Rate Law:

## Example:

For the reaction:  $A \rightarrow \text{Products}$

$$\text{Avg. Rate} = \frac{\Delta[A]}{\Delta t}$$

The rate of consumption of  $A$  is **DIRECTLY PROPORTIONAL** to its **CONCENTRATION**.

- i.e. the **FASTER**  $A$  is **CONSUMED**, the **LOWER** its **CONCENTRATION**.

This is represented by the equation:

$$\text{Rate} = k[A]^x$$

Where:

$k$  is the **RATE CONSTANT**

$[A]$  is the **CONCENTRATION** of  $A$

$x$  is a power, called the **ORDER OF THE REACTION**

# Rate Law:

## The Rate Constant (k):

- Can only be determined **EXPERIMENTALLY**.
- Is **SPECIFIC** for each **REACTION** at a specific **TEMPERATURE**, since its value depends on the **SIZE**, **SPEED** and **TYPE** of molecules.
- Changing **TEMPERATURE** changes **SPEED** of reactant molecules, which changes **RATE CONSTANT**.
- **TEMPERATURE** is the **ONLY FACTOR** that **AFFECTS** the rate **CONSTANT**

# Order of Reaction:



$$\text{RATE} = k [A]^x$$

## Reaction Order:

Indicates how the **CONCENTRATION** of reactants **AFFECTS** the **RATE** of the reaction. Can only be determined **EXPERIMENTALLY**.

$$\text{Rate} = k [A]^1$$

$$\begin{aligned} \text{Rate} &= k(1)^1 \\ &= 1k \end{aligned}$$

$$\begin{aligned} \text{Rate} &= k(2)^1 \\ &= 2k \end{aligned}$$

## ***First Order Reactions (X = 1)***

- The reaction rate is **DIRECTLY PROPORTIONAL** to changes in reactant **CONCENTRATION**.
- If reactant concentration were:

- **DOUBLED**, the rate would **DOUBLE**

- **TRIPLED**, the rate would **TRIPLE**, etc

$$\begin{aligned} \text{RATE} &= k(3)^1 \\ &= 3k \end{aligned}$$



# Order of Reaction:

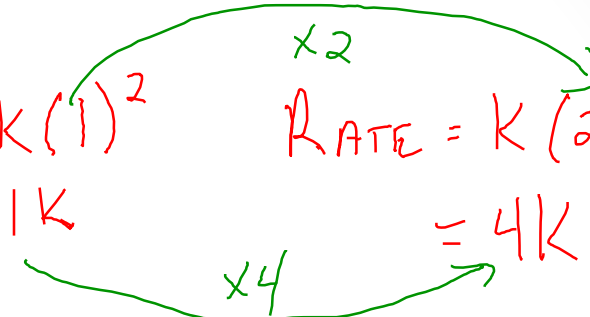
## **Second Order Reactions (X = 2)**

- **DOUBLING** the concentration would **QUADRUPLE** the rate.
  - i.e.  $2^x = 2^2 = 4$
- **TRIPLING** the concentration would **INCREASE** the rate by a **FACTOR** of **9**:
  - i.e.  $3^x = 3^2 = 9$

$$\text{RATE} = k[A]^2$$

$$\begin{aligned} \text{RATE} &= k(1)^2 \\ &= 1k \end{aligned}$$

$$\begin{aligned} \text{RATE} &= k(2)^2 \\ &= 4k \end{aligned}$$



## **Zero Order Reaction (X = 0)**

- Here, a change in **CONCENTRATION** will **NOT AFFECT** the **RATE** of the reaction.
  - i.e.  $2^x = 2^0 = 1$

$$\text{RATE} = k[A]^0 = k(1 \times 10^{23})^0 = 9k$$

$$\text{Rate} = k(3)^2$$

= k

## Order of Reaction:

	<b>Order of Reaction (exponent)</b>			
<b>Conc. Change</b>	<b>0</b>	<b>1</b>	<b>2</b>	<b>3</b>
<b>x1</b>	$1^0 = 1$	$1^1 = 1$	$1^2 = 1$	$1^3 = 1$
<b>x2 (doubling)</b>	$2^0 = 1$	$2^1 = 2$	$2^2 = 4$	$2^3 = 8$
<b>x3 (tripling)</b>	$3^0 = 1$	$3^1 = 3$	$3^2 = 9$	$3^3 = 27$

# Rate law & Order of Reaction:

## Example:

For a reaction with more than one reactant:



The rate law would be:

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

The rate depends on both **[A] and [B]**. Each reactant can affect the rate **DIFFERENTLY**.

The ***total order of the reaction*** is the **SUM** of the **EXPONENTS** in the **RATE LAW**.



# Determining Rate Law:

## Determining Rate Law – Initial Rate Method:

- Can only be done **EXPERIMENTALLY**.
- Even though rate does depend on stoichiometry to an extent, the rate law cannot be determined from **COEFFICIENTS**.
- We can **MEASURE** the effect on changes in concentration of one reactant on the rate by keeping the other reactant concentration **CONSTANT**.

# Determining Rate Law:

## Example:

What is the rate law for the following reaction, given the following experimental data?



Trial Number	[H <sub>2</sub> O <sub>2</sub> ] (mol/L)	[HI] (mol/L)	Rate (mol/L·s)
1	0.10	0.10	0.0076
2	0.10	0.20	0.0152
3	0.20	0.10	0.0152

$$2^1 = 2$$

$$\text{RATE} = k [\text{H}_2\text{O}_2]^1 [\text{HI}]^1$$

Trials 1 & 3, [HI] = const, [H<sub>2</sub>O<sub>2</sub>] × 2, Rate × 2

$$2^1 = 2$$

∴ 1<sup>st</sup> order in [H<sub>2</sub>O<sub>2</sub>]

Trials 1 & 2, [H<sub>2</sub>O<sub>2</sub>] = const, [HI] × 2, Rate × 2

$$2^1 = 2$$

∴ 1<sup>st</sup> order in [HI]

# Determining Rate Law:

## Example:

Find the rate law for the reaction:  $2\text{NO}_{2(g)} + \text{F}_{2(g)} \rightarrow 2\text{NO}_2\text{F}_{(g)}$

[NO <sub>2</sub> ] (mol/L)	[F <sub>2</sub> ] (mol/L)	Rate (mol/L·s)
0.0010	0.0010	0.4
0.0010	0.0030	1.2
0.0050	0.0030	6.0
0.0050	0.0050	10

$$5^x = 5$$
$$x = 1$$

$$3^x = 3$$
$$x = 1$$

$$\text{RATE} = k [\text{NO}_2]^1 [\text{F}_2]^1$$

# Determining Rate Law:

Try this one...

When the reaction  $\text{CH}_3\text{Cl}_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CH}_3\text{OH}_{(g)} + \text{HCl}_{(g)}$  was studied, the following data was obtained:

3rd order

Trial	$[\text{CH}_3\text{Cl}]$ (mol/L)	$[\text{H}_2\text{O}]$ (mol/L)	Initial Rate (mol/L·s)
1	0.100	0.100	0.182
2	0.200	0.100	1.45
3	0.200	0.400	5.81

Q

$2^x = 8$   
 $x = 3$

$4^x = 4$   
 $x = 1$

Determine the rate law for this reaction...

$$\text{RATE} = k [\text{CH}_3\text{Cl}]^3 [\text{H}_2\text{O}]^1$$

# Finding the Value of K:

Once we have found the rate law for a reaction, we can find the value of the rate constant  $k$ . Simply **SUBSTITUTE** the data from **ANY TRIAL** into the rate law and solve for  $k$ .

## Example:

For the reaction:  $3A_{(g)} + B_{(g)} + 2C_{(g)} \rightarrow 2D_{(g)} + 3E_{(g)}$  the following data was obtained:

Trial	[A](mol/L)	[B] (mol/L)	[C] (mol/L)	Rate (mol/Ls)
1	0.10	0.10	0.10	0.20
2	0.20	0.10	0.10	0.40
3	0.20	0.20	0.10	1.60
4	0.20	0.10	0.20	0.40
5	0.50	0.40	0.25	??
6	??	0.60	0.50	6.00

$$\begin{aligned} 2^1 &= 2 \\ 2^2 &= 4 \\ 2^0 &= 1 \end{aligned}$$

a) Determine the Rate Law:

$$R_{\text{ATE}} = k [A]^1 [B]^2 [C]^0$$

$$R_{\text{ATE}} = k [A]^1 [B]^2$$

# Finding the Value of K:

$$\left(\frac{\text{mol}}{\text{L}}\right) \left(\frac{\text{mol}}{\text{L}}\right)^2 = \frac{\text{mol}}{\text{L}} \times \frac{\text{mol}}{\text{L}} \times \frac{\text{mol}}{\text{L}}$$

## Example (con't):

Trial	[A](mol/L)	[B] (mol/L)	[C] (mol/L)	Rate (mol/Ls)
1	0.10	0.10	0.10	0.20
2	0.20	0.10	0.10	0.40
3	0.20	0.20	0.10	1.60
4	0.20	0.10	0.20	0.40
5	0.50	0.40	0.25	??
6	??	0.60	0.50	6.00

b) Calculate the value of the rate constant.

$$\text{RATE} = k[A]^1[B]^2$$

$$\frac{0.2 \frac{\text{mol}}{\text{L}\cdot\text{s}}}{\left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right) \left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right)^2} = k \frac{\left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right) \left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right)^2}{\left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right) \left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right)^2}$$

$$k = \frac{0.2 \frac{\text{mol}}{\text{L}\cdot\text{s}}}{\left[\left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right) \left(\frac{0.1 \frac{\text{mol}}{\text{L}}\right)^2\right]}$$

$$k = 200$$

$$\left(\frac{\text{mol}}{\text{L}\cdot\text{s}}\right) \frac{1}{\left(\frac{\text{mol}}{\text{L}}\right) \left(\frac{\text{mol}}{\text{L}}\right)^2} = \frac{\text{mol}}{\text{L}\cdot\text{s}} \frac{\text{L}^3}{\text{mol}^3} = \frac{\text{mol}}{\text{L}\cdot\text{s}} \times \frac{\text{L}^3}{\text{mol}^3} = \frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}}$$

c) Calculate the rate for trial #5.

$$\begin{aligned} \text{RATE} &= 200 [A][B]^2 \\ &= 200 (0.5)(0.4)^2 \\ &= 16 \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$

d) Calculate the concentration of A in trial #6.

$$\begin{aligned} \text{RATE} &= 200 [A][B]^2 \\ 6 &= 200 [A](0.6)^2 \end{aligned}$$

$$\begin{aligned} [A] &= \frac{6}{(200)(0.6)^2} \\ [A] &= 0.083 \frac{\text{mol}}{\text{L}} \end{aligned}$$