

# **KINETICS**

## **2: CALCULATING RATE LAW**

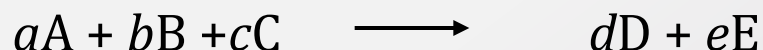
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# RATE LAW – CONCENTRATION CHANGES

Rate of reaction is dependent on the concentration of reactants.

- Rate of reaction is then given by the rate law. This is an equation that relates rate of reaction to the concentration of a reactant raised to various powers. The proportionality constant,  $k$ , is the rate constant.

For the generic reaction



the rate law is

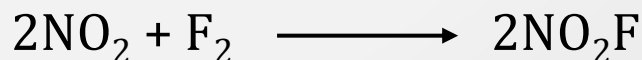
$$\text{Rate} = k[A]^x[B]^y[C]^z$$

- Where  $k$  = rate constant (specific for the reaction at a particular temp.)
- $xyz$  are integers and called order of reaction (calculated experimentally).
- $x+y+z$  is the overall order of reaction.

# ORDER OF REACTION

- **0 order** - changing the conc. of reactants does not affect rate of reaction.
- **1st order** - rate directly proportional to concentration – i.e. if you double the concentration, you double the rate of reaction.
- **2nd order** - exponential relationship – i.e. if you double the concentration, you quadruple the rate of reaction.
- Sum of exponents (order) indicates overall reaction order

For example, for the reaction below:



The rate equation was determined to be:  $\text{Rate} = k [\text{NO}_2][\text{F}_2]$

This means order of reactions are 1 for both  $\text{NO}_2$  and  $\text{F}_2$  (we can write either 1 or no integer to represent 1).

Overall order is 2.

Another example: If the orders for the reaction above were 2 for  $\text{NO}_2$  and 0 for  $\text{F}_2$ , the rate equation will be:  $\text{Rate} = k [\text{NO}_2]^2$ .

If a reactant is zero order it is not part of rate equation. Overall order is 2.

# DETERMINING ORDER OF REACTION

This can be done only experimentally. To obtain order of reaction, a series of reactions have to be performed in quantitative manner. Quantitative data could be change in concentration, change in pH or voltage etc.

- Depending on the number of reactants, one reactant is kept constant and the other concentration is changed and monitored what happens to the rate of reaction.
- The process is then reversed i.e., keep the concentration of second one constant and change the first one and monitor for change of rate of reaction.
- Once data is obtained calculate the order of reaction.
- The value of “ $k$ ” can also be calculated after obtaining the orders of reaction.

# EXAMPLE 1: ORDER OF REACTION

For a reaction between  $F_2$  and  $ClO_2$ , reaction rate data was collected as given in the table below. Calculate the rate constant of the reaction.

| Exp. | $[F_2]$ (M) | $[ClO_2]$ (M) | Initial Rate (M/s)   |
|------|-------------|---------------|----------------------|
| 1    | 0.10        | 0.010         | $1.2 \times 10^{-3}$ |
| 2    | 0.10        | 0.040         | $4.8 \times 10^{-3}$ |
| 3    | 0.20        | 0.010         | $2.4 \times 10^{-3}$ |

**Answer:** To find the rate constant,  $k$ , first find rate equation (order of reaction).

1) Find order (exponents) by comparing data Exp. 1 and 2:  $[F_2]$  is held constant

$$\frac{[ClO_2]_2}{[ClO_2]_1} = \frac{0.040M}{0.010M} = 4 \quad \frac{[rate]_2}{[rate]_1} = \frac{4.8 \times 10^{-3}M/s}{1.2 \times 10^{-3}M/s} = 4$$

*Rate increases 4 times when conc. increases by a factor of 4 – 1<sup>st</sup> order with respect to  $ClO_2$ .*

2) Find order (exponents) by comparing data Exp. 1 and 3:  $[ClO_2]$  is held constant

$$\frac{[F_2]_3}{[F_2]_1} = \frac{0.20M}{0.10M} = 2 \quad \frac{[rate]_3}{[rate]_1} = \frac{2.4 \times 10^{-3}M/s}{1.2 \times 10^{-3}M/s} = 2$$

*Rate increases 2 times when conc. increases by a factor of 2 – 1<sup>st</sup> order with respect to  $F_2$ .*

**3) Rate =  $k [F_2]^1 [ClO_2]^1$  overall order = 2**

4)  $k = \text{Rate} / [F_2]^1 [ClO_2]^1 = 1.2 \times 10^{-3} M/s / (0.1M)(0.01M) = \mathbf{1.2 M^{-1}s^{-1}}$

# EXAMPLE 2: ORDER OF REACTION

Let's find the order of reaction without detailed calculations to find  $k$ .

| Exp. | [A]  | [B]   | Initial Rate (M/s)   |
|------|------|-------|----------------------|
| 1    | 0.10 | 0.015 | $2.1 \times 10^{-4}$ |
| 2    | 0.20 | 0.015 | $4.2 \times 10^{-4}$ |
| 3    | 0.10 | 0.030 | $8.4 \times 10^{-4}$ |

- In experiment 1 and 2; [B] is constant; [A] doubles and rate doubles - the reaction is 1st order with respect to [A]
- In experiment 1 and 3; [A] is constant; [B] doubles but the rate quadruples! This means that the reaction is 2nd order with respect to [B]
- $\text{Rate} = k [\text{A}] [\text{B}]^2$

$$k = \frac{[\text{rate}]}{[\text{A}][\text{B}]^2} = \frac{2.1 \times 10^{-4} \text{ M/s}}{(0.10 \text{ M})(0.015 \text{ M})^2} = \boxed{9.3 \text{ M}^{-2} \text{ s}^{-1}}$$

# UNITS OF RATE CONSTANT

Note that the units on the rate constant are specific to the overall order of the reaction.

- For a zero-order reaction, the unit is  $M/s$  or  $\text{mol}/(\text{L} \cdot \text{s})$ .

$$\text{Rate} = k$$

- For a first-order reaction, the unit is  $1/s$  or  $s^{-1}$ .

$$\text{Rate} = k[A]; \quad k = \frac{\text{Rate } Ms^{-1}}{[A]M} = s^{-1}$$

- For a second-order reaction, the unit is  $1/(M \cdot s)$  or  $\text{L}/(\text{mol} \cdot \text{s})$ .

$$\text{Rate} = k[A]^2; \quad k = \frac{\text{Rate } Ms^{-1}}{[A]M \times [A]M} = M^{-1}s^{-1}$$

If you know the rate constant, you can deduce the overall rate of reaction

# KEY CONCEPTS

- Calculate order of reactions