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

$$aA + bB + cC \longrightarrow dD + eE$$

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:

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

The rate equation was determined to be: Rate = $k\,[NO_2][F_2]$

This means order of reactions are 1 for both NO_2 and 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 NO_2 and 0 for F_2, the rate equation will be: Rate = $k\,[NO_2]^2$.

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	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-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

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

Rate increases 4 times when conc. increases by a factor of 4 – 1st order with respect to ClO_2.

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

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

Rate increases 2 times when conc. increases by a factor of 2 – 1st order with respect to F_2.

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

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

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	2.1×10^{-4}
2	0.20	0.015	4.2×10^{-4}
3	0.10	0.030	8.4×10^{-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]
- Rate = k [A] $[B]^2$

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

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 mol/(L·s).

  Rate = k

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

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

- For a second-order reaction, the unit is 1/(M·s) or L/(mol·s).

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

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

KEY CONCEPTS

- Calculate order of reactions