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Topic 5.2: Introduction to Rate Law

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UNIT 5 · KINETICS

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The Rate Law: Rate Written in Terms of Concentration

A rate law links the rate of a reaction to the reactant concentrations at that moment.

For A and B it takes the form rate = $k[A]^m[B]^n$. The square brackets mean concentration in mol/L, written M.

The constant k is the rate constant. At a fixed temperature it has one value for a given reaction, and it does not change when the concentrations change.

The powers m and n are the orders of the reaction: the power on [A] is the order with respect to A, and the power on [B] is the order with respect to B.

The overall order is the sum of the individual orders, m + n.

What an Order Means

An order tells you the factor by which the rate changes when one concentration changes and the others are held constant.

Zero order means the rate does not depend on that concentration at all. Doubling or halving it leaves the rate unchanged, because $[A]^0 = 1$ and the term drops out of the rate law.

First order means the rate is directly proportional to the concentration. Double the concentration and the rate doubles; halve it and the rate halves.

Second order means the rate depends on the square of the concentration. Double the concentration and the rate multiplies by $2^2 = 4$; triple it and the rate multiplies by $3^2 = 9$.

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Orders Come From Experiment, Never From the Equation

Orders are measured, not calculated: run the reaction, change one concentration at a time, and record how the initial rate responds.

They cannot be read from the balanced equation. In $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ the coefficient of NO is 2 and experiment happens to give second order in NO, but that agreement is a coincidence of this reaction, not a rule.

Another reaction with a coefficient of 2 can be first or zero order in that species. Coefficients come from balancing atoms; orders come from data.

The Method of Initial Rates

The standard experiment measures the initial rate, at the start of each run, while the concentrations are still the known starting values.

Several runs are made with different starting concentrations. To find the order in A, choose two runs in which [A] changes and [B] is the same, so any change in rate must be caused by [A] alone.

Compare the runs as ratios. If [A] changes by a factor of 2 and the rate by a factor of 4, then 2 raised to the order gives 4, so the order is 2.

Repeat with a pair changing only [B] to find the order in B. Once both orders are known, any one run substituted into the rate law gives k.

The Rate Constant k and Its Units

Once the orders are known, k comes from any single experiment: $k = \text{rate} \div ([A]^m[B]^n)$, substituting that run's numbers.

The units of k depend on the overall order, because k must turn the concentration terms into a rate in M/s.

For an overall order of zero, rate = k, so k carries the units of rate itself: $M\ s^{-1}$. For overall first order, rate = k[A], so $k = (M/s) \div M = s^{-1}$.

For overall second order, $k = (M/s) \div M^2 = M^{-1}\ s^{-1}$. For overall third order, $k = (M/s) \div M^3 = M^{-2}\ s^{-1}$.

The pattern is k has units M^(1 − overall order) s^{-1}, so the units of a given k reveal the overall order: s^{-1} means first order overall, $M^{-1}\ s^{-1}$ means second.

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Temperature is the change that alters k. Raising the temperature increases k, so the same concentrations give a faster rate. Changing a concentration changes the rate, but k itself stays exactly the same.

Worked Examples

Example 1: Orders, k and a prediction from one table. For A + B → products, three initial rate runs give: [A] = 0.10 M, [B] = 0.10 M, rate = 4.0×10^{-3} M/s; [A] = 0.20 M, [B] = 0.10 M, rate = 1.6×10^{-2} M/s; [A] = 0.10 M, [B] = 0.20 M, rate = 8.0×10^{-3} M/s. Between the first two runs [A] doubles at constant [B] and the rate multiplies by 4, so the reaction is second order in A. Between the first and third runs [B] doubles and the rate doubles, so it is first order in B. The rate law is rate = $k[A]^2[B]$, with overall order 3. Using the first run, $k = 4.0 \times 10^{-3} \div ((0.10)^2 \times 0.10) = 4.0 \times 10^{-3} \div 1.0 \times 10^{-3} = 4.0\ M^{-2}\ s^{-1}$. At [A] = 0.30 M and [B] = 0.20 M the predicted rate is $4.0 \times (0.30)^2 \times 0.20 = 0.072$ M/s.

Example 2: A zero order hiding in the data. For E + F → products, the runs give: [E] = 0.10 M, [F] = 0.10 M, rate = 3.0×10^{-3} M/s; [E] = 0.10 M, [F] = 0.30 M, rate = 3.0×10^{-3} M/s; [E] = 0.30 M, [F] = 0.10 M, rate = 9.0×10^{-3} M/s. Tripling [F] at constant [E] changes nothing, so the order in F is 0 and F does not appear in the rate law. Tripling [E] triples the rate, so the order in E is 1. The rate law is rate = k[E], overall order 1, and $k = 3.0 \times 10^{-3} \div 0.10 = 0.030\ s^{-1}$, the first order unit.

Example 3: Combining two changes at once. A reaction follows rate = $k[NO]^2[O_2]$ and has an initial rate of 1.6×10^{-3} M/s in one run. In a second run [NO] is doubled and $[O_2]$ is halved. Doubling [NO] multiplies the rate by 4 and halving $[O_2]$ by 1/2, so the combined factor is 2 and the new rate is 3.2×10^{-3} M/s. No value of k is needed: k is the same in both runs and cancels.

Example 4: Reading the overall order from the units of k. A rate constant is reported as 0.25 $M^{-1}\ s^{-1}$. Matching $M^{-1}\ s^{-1}$ against the pattern M^(1 − overall order) s^{-1} gives 1 − overall order = −1, so the overall order is 2. At [A] = 0.40 M in rate = $k[A]^2$, the rate is $0.25 \times (0.40)^2 = 0.040$ M/s, and the units check: $M^{-1}\ s^{-1} \times M^2 = M/s$.

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Traps That Cost Marks in Topic 5.2

Reading orders from coefficients. A coefficient in the balanced equation is not an order. Orders come only from initial rate experiments; writing rate = $k[A]^2[B]$ just because the equation shows 2A + B is the most common error in this topic.

Comparing runs that change two things. If both [A] and [B] differ between two runs, the rate ratio mixes both effects. Always pick the pair that holds one concentration constant.

Giving k without its units, or with the wrong ones. The units of k change with the overall order. A third order k in s^{-1} is wrong even if the number is right; it must be $M^{-2}\ s^{-1}$.

Treating a zero order reactant as absent from the reaction. Zero order means the rate does not respond to that concentration. The species is still consumed; it simply does not appear in the rate law.

Claiming a concentration change alters k. Doubling [A] changes the rate through the rate law; k is untouched. Only a temperature change alters k.

Mishandling the factor. Tripling a second order concentration multiplies the rate by 9, not by 6 or 3. Apply the order as a power to the concentration factor.

Key Relationships to Remember

- Rate law: rate = $k[A]^m[B]^n$, where m and n are the orders in A and B, found from experiment only
- Overall order = m + n, the sum of the individual orders
- Doubling a concentration multiplies the rate by 2^(order): factor 1 for zero order, 2 for first order, 4 for second order
- Method of initial rates: compare two runs that differ in one concentration only; the rate ratio gives that reactant's order
- k = rate ÷ ($[A]^m[B]^n$) from any one run once the orders are known; k is constant at constant temperature and independent of concentration
- Units of k: M^(1 − overall order) s^{-1}, so $M\ s^{-1}$ for zero order, s^{-1} for first, $M^{-1}\ s^{-1}$ for second, $M^{-2}\ s^{-1}$ for third
- Raising the temperature increases k; changing concentrations changes the rate but leaves k unchanged

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