

Rate Laws & Reaction Order

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Reaction Order

A Little Review

- To this point we have looked at data that represents the relationship between concentration and time.

Rate Data for Reaction of C_4H_9Cl with Water

TABLE 14.2 Rate Data for Reaction of C_4H_9Cl with Water

Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

- From this data, we have discussed the average and instantaneous rates of change

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Reaction Order

Moving On...

- We are now ready to look at the factors that affect reaction rates and how we represent these affects mathematically
- To do this, let's consider another reaction.....
- $\text{NH}_4^{+1} + \text{NO}_2^{-1} \Rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$

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Table 14.3

Rate Data for the Reaction of Ammonium and Nitrite Ions

TABLE 14.3 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

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

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Reaction Order

Rate Law

- Increasing the concentration of either the NH_4^{+1} or the NO_2^{-1} affects a proportional change on the rate of the reaction.
- We can represent this relationship mathematically
 - $\text{Rate} = k[\text{NH}_4^{+1}][\text{NO}_2^{-1}]$
- This is termed the **rate law** for this reaction
 - Represents the relationship between concentration and rate for a chemical reaction
 - k is the rate constant
- Using the data in the previous table, let's find k for this reaction
- Using this information, we can calculate the rate for this reaction at any set of given concentrations

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Reaction Order

Reaction Order

- The rate law for most reactions can be expressed as
- $\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$
- m and n are termed reaction orders
 - Represent the relationship between [conc] and rate
 - Zero order = [conc] x2, rate unchanged
 - 1st order = [conc] x2, rate x 2
 - 2nd order = [conc] x2, rate x 4
 - 3rd order = [conc] x2, rate x 8
- Their sum is termed the overall reaction order
- In the previous reaction, what is the reaction order for NH_4 and NO_2 ?
- What is the overall reaction order?
- Notice that the reaction order cannot be predicted by looking at the balanced chemical reaction. The reaction order (the relationship between concentration and rate) must be found experimentally
- Let's look at another example...

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Reaction Order

Reaction Order

- Let's solve exercise 14.6 on page 568

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Reaction Order

Reaction Mechanisms

- To understand why stoichiometric relationships are not a predictor of reaction order, we need to understand the processes that occur when reactions take place.
- These processes are termed **reaction mechanisms**
 - Provide information regarding the order in which bonds are broken and formed

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Reaction Order

Reaction Mechanisms

- $A + B \implies C$
 - $A \implies A_1 + A_2$
 - $A_1 + B \implies A_1B$
 - $A_1B + A_2 \implies C$
- Reaction mechanisms can be broken into elementary steps
 - The single steps that add up to the complete reaction mechanism
 - Described by the number of molecules acting as reactants
 - Molecularity
 - Unimolecular - one molecule breaking apart or rearranging
 - Bimolecular - involves the collision of two molecules
 - Termolecular - involves the collision of three molecules
 - Not very likely - rarely occur
 - More than three aren't generally used because they are so nonprobable
- These elementary steps are then added together to create a complete reaction mechanism

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Reaction Order

Homework

- 14.27 / 14.28 / 14.29 / 14.33 / 14.35 / 14.37