Chapter 12 Part 2

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Rate Laws

- Describes the relationship between the rate of a reaction and the molar concentrations of the chemical reactants
- For the reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \cdots \rightarrow g\,\mathrm{G} + h\,\mathrm{H} \cdots,$$

$$\text{rate} = k[\mathrm{A}]^m[\mathrm{B}]^n \cdots$$

- [A] and [B] are the molar concentrations of the reactants
- k is the rate constant. The rate constant is specific only works for a particular reaction at a certain temperature and surface area.

Reaction Order

$$\text{rate} = k[\text{A}]^m[\text{B}]^n \cdots$$

- The exponents m and n must be determined experimentally by observing how the rate of a reaction changes as the concentration of the reactants are changed
- The exponent of a particular reactant is the order of the reaction with respect to that reactant
- The sum of all of the exponents is the overall reaction order

Reaction Order

For a reaction with the rate law: rate $= k[\mathrm{KOH}]^3[\mathrm{H_3PO_4}]$, what is the order of the reaction with respect to KOH?

A. 1
B. 2
C. 3
D. 4

Reaction Order

For a reaction with the rate law: rate $= k[\mathrm{KOH}]^3[\mathrm{H_3PO_4}]$, what is the overall order of the reaction?

A. 1
B. 2
C. 3
D. 4

Determining the rate law from initial rates

$$\left(\frac{[\mathrm{A}]_i}{[\mathrm{A}]_j}\right)^m = \frac{\mathrm{rate}_i}{\mathrm{rate}_j}$$

- $[\mathrm{A}]_i$ is the concentration of reactant A during experiment i.
- $[\mathrm{A}]_j$ is the concentration of reactant A during experiment j.
- m is the order of the reaction with respect to A.
- rate_i is the rate of experiment i.
- rate_j is the rate of experiment j.

Method of Initial Rates

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

Experiment	Initial [NO]	Initial [O_2]	Initial Rate of Formation of NO_2 (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

A. Determine the rate law (in terms of *k*)

Method of Initial Rates

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B. Calculate the rate constant

Method of Initial Rates

At 60 °C, acetone (CH_3COCH_3) decomposes to ketene ($CH_2{=}C{=}O$) and various hydrocarbons. Initial rate data are given in the table:

Experiment	Initial $[CH_3COCH_3]$	Initial Rate of Decomposition of CH_3COCH_3 (M/s)
1	6.0×10^{-3}	5.2×10^{-5}
2	9.0×10^{-3}	7.8×10^{-5}

A. Determine the rate law (in terms of k)

B. Calculate the rate constant.

C. Calculate the rate of decomposition when the acetone concentration is 1.8×10^{-5}.

Method of Initial Rates

$$2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$$

Experiment	[NO]	$[Cl_2]$	Rate (M/s)
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

A. Determine the rate law (in terms of k)

B. Calculate the rate constant

C. Calculate the rate when the concentrations are $[NO] = 0.300$ M and $[Cl_2] = 0.400$ M.

Rate Constants for Common Overall Reaction Orders

Reaction Order	Units of k
Zero	$\frac{\mathrm{M}}{\mathrm{s}}$
First	$\frac{1}{\mathrm{s}}$
Second	$\frac{1}{\mathrm{M\,s}}$
Third	$\frac{1}{\mathrm{M^2\,s}}$
$(m+n)$	$\frac{1}{\mathrm{M}^{(m+n-1)}\,\mathrm{s}}$