

Chemical Kinetics

these gases can exist indefinitely at 25°C



Many chemical reactions are spontaneous.

but very slow

It is not enough to understand the stoichiometry and thermodynamics of a chemical reaction we must also understand the factors that govern the **rate of reaction.**

Chemical Kinetics

the study of the rate at which chemical reactions take place

gives us clues as to the reaction

mechanism : the pathway by which reactants are converted to products

Kinetics: concerned with systems before equilibrium is reached

Balanced Equations can be Deceiving:

many chemical reactions don't proceed in a straightforward single step as suggested by their balanced equation



**Implies a collision of nine molecules
simultaneously!**

Extremely unlikely event

Factors affecting the rate of reaction

Nature of the reactants

Surface area of reactants

Presence of a catalyst

increases the reaction rate but can be recovered in its original form at the end of the reaction

Temperature of the system

Concentration of reactants

**Rate of reaction for a
homogeneous reaction (single
liquid or gas)**

**Usually depends on the concentration of the
reactants.**

**Rate of reaction for a
heterogeneous reaction (more
than one phase)**

**May depend on the surface area of contact
between the phases.**

Rate of Reaction

Reaction rate

Change in concentration of a reactant or product with time

$$\text{Rate} = \frac{C_f - C_i}{t_f - t_i} = \frac{\Delta C}{\Delta t}$$

Products increase

$$\Delta[\text{products}]/\Delta t$$

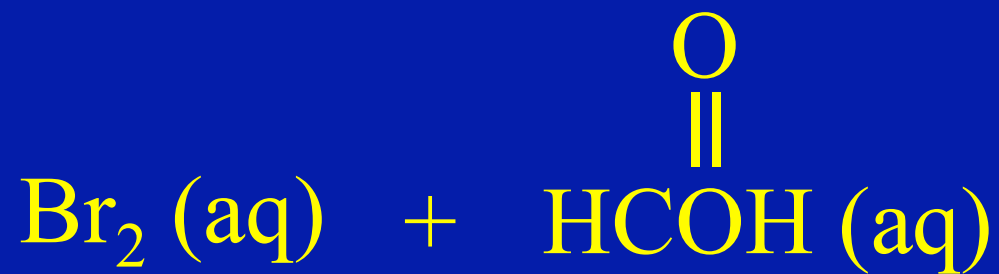
$$d[\text{products}]/dt$$

Reactants decrease

$$-\Delta[\text{reactants}]/\Delta t$$

$$-d[\text{reactants}]/dt$$

Reaction of Molecular Bromine and Formic Acid



How is the rate of a reaction
expressed?

Average rate

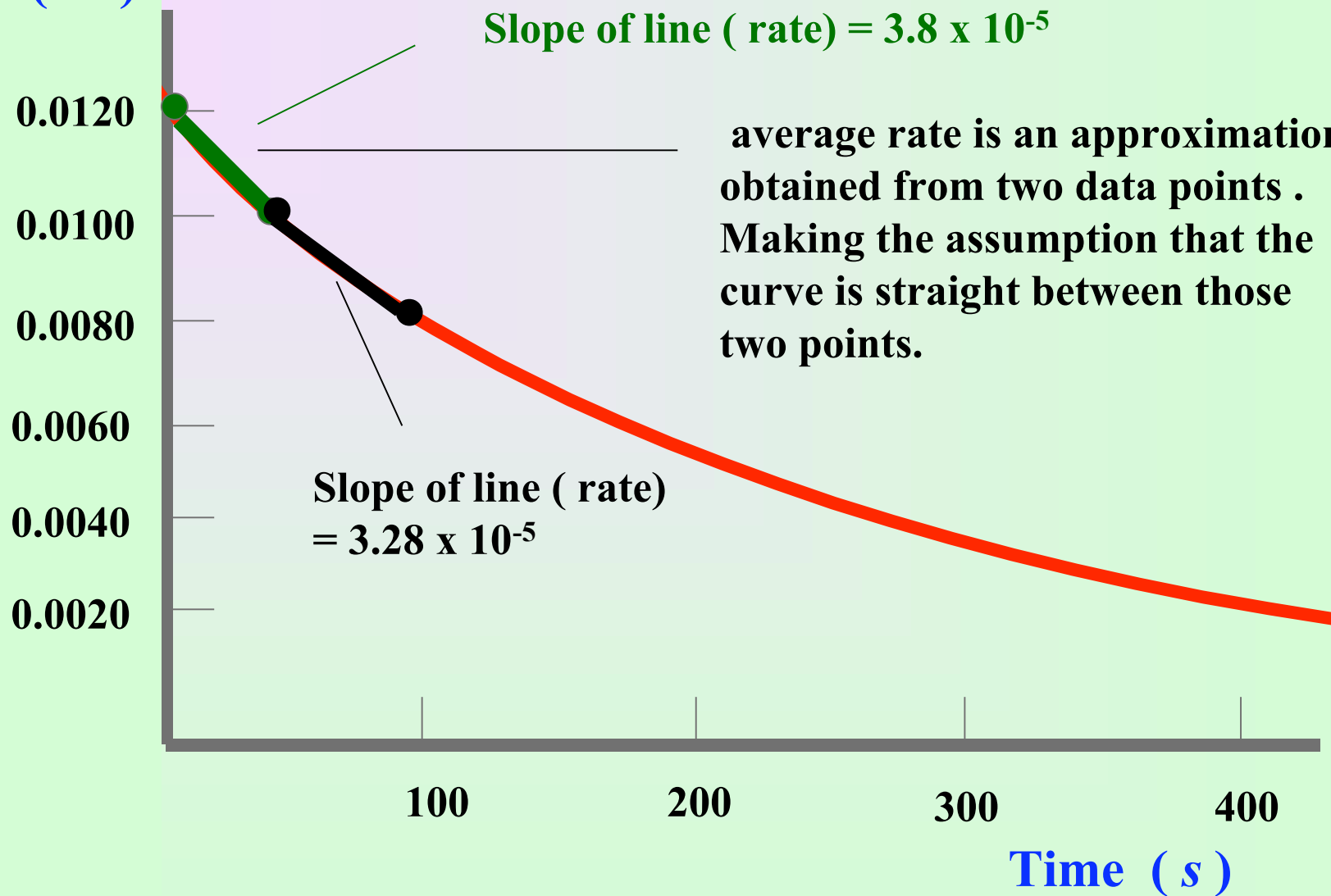
Time (s)	[Br ₂] mol/L	Average Rate (M/s)
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0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353

3.8×10^{-5}

$$\frac{\Delta[\text{Br}_2]}{\Delta t}$$

$[\text{Br}_2] \text{ (M)}$

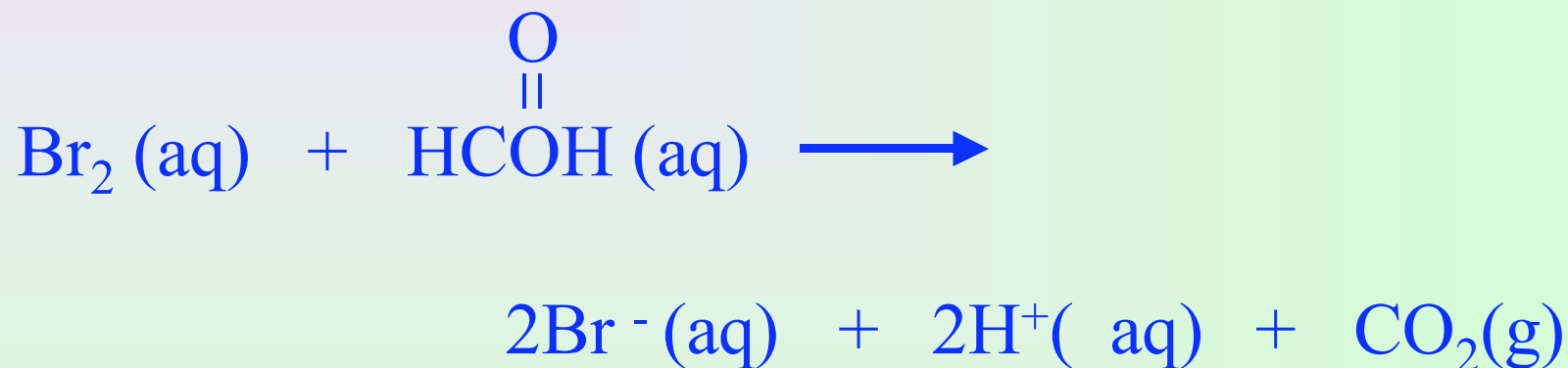


The value of reaction rate depends on which reactant or product is measured.

After the rate has been measured based on one component of the reaction, the rates of the other components may be calculated by a stoichiometric conversion

Example

What will the rate of production H^+ be if the the rate of consumption Br_2 is $3.8 \times 10^{-5} \text{ mol/Ls}$



$$\frac{3.8 \times 10^{-5} \text{ mol Br}_2}{\text{Ls}} \times \frac{2 \text{ mol H}^+}{1 \text{ mol Br}_2} = \frac{7.6 \times 10^{-5} \text{ mol H}^+}{\text{Ls}}$$

Time (s)	[Br ₂] mol/L	Average Rate (M/s)
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0.0	0.0120	3.8 x 10 ⁻⁵
50.0	0.0101	3.28 x 10 ⁻⁵
100.0	0.00846	2.72 x 10 ⁻⁵
150.0	0.00710	2.28 x 10 ⁻⁵
200.0	0.00596	1.92 x 10 ⁻⁵
250.0	0.00500	1.60 x 10 ⁻⁵
300.0	0.00420	1.34 x 10 ⁻⁵
350.0	0.00353	

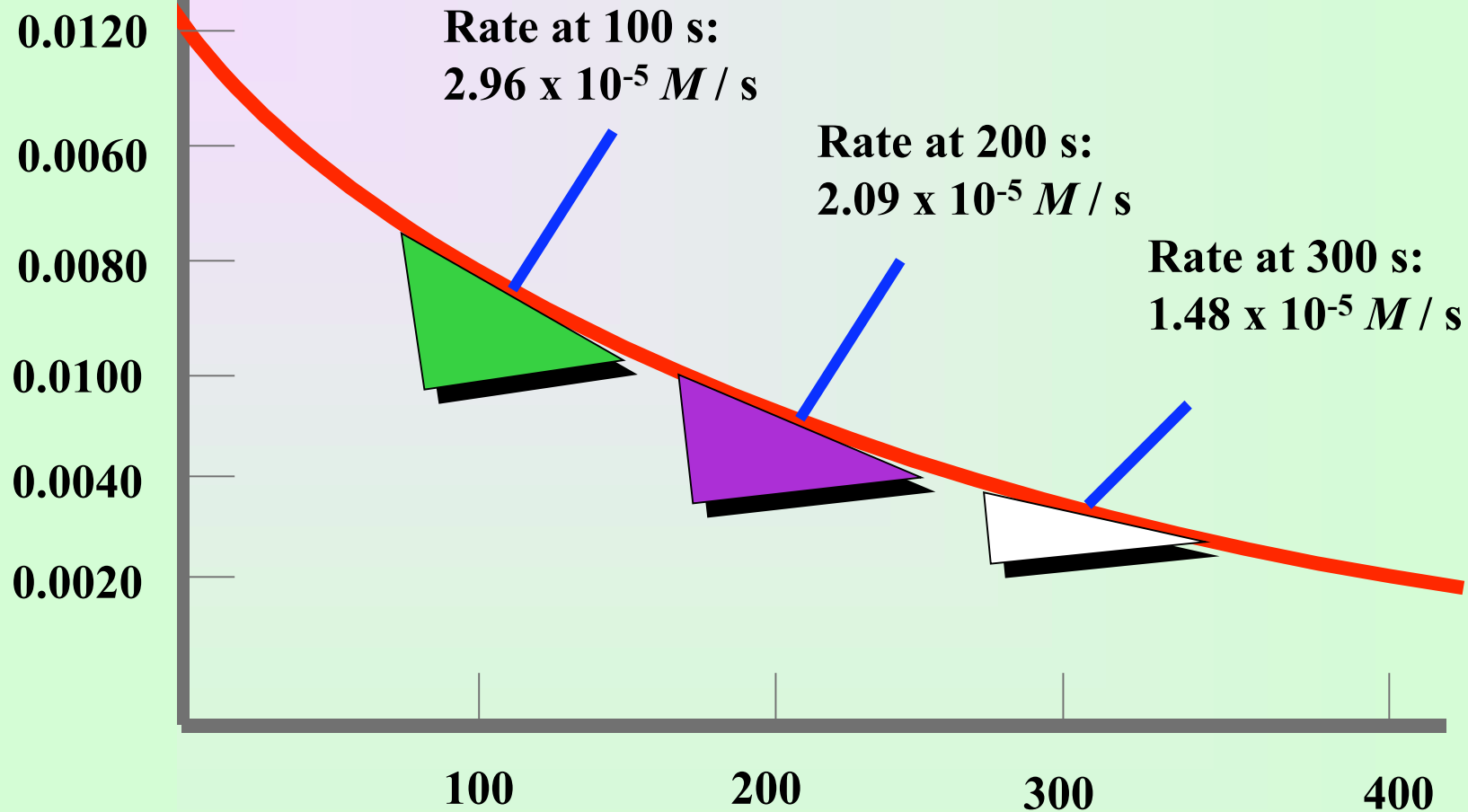
$$\frac{\Delta[\text{Br}_2]}{\Delta t}$$

How is the rate of a reaction
expressed?

Average rate

Instantaneous rate

$[\text{Br}_2]$ (M)



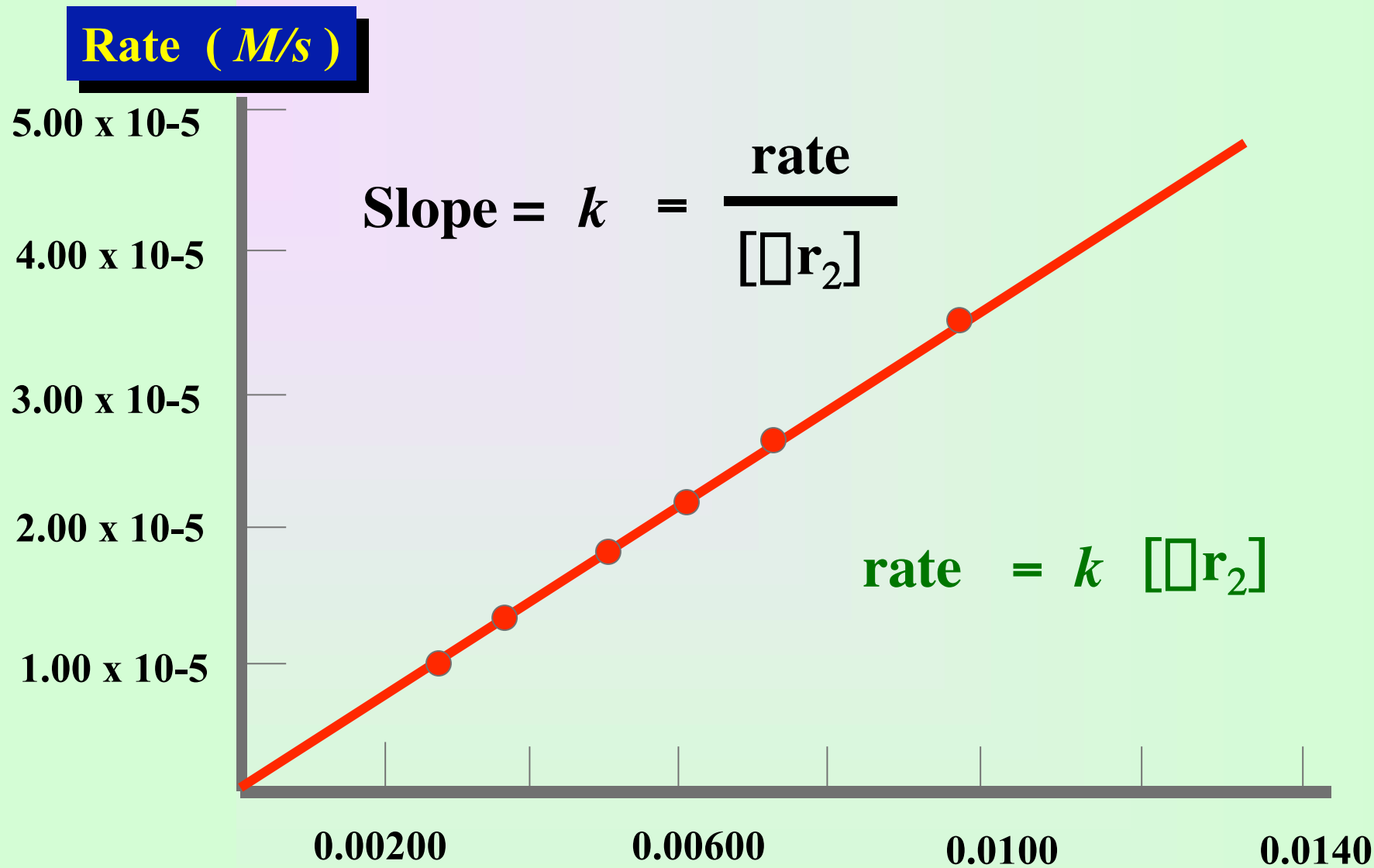
The instantaneous rates of Br_2 and formic acid at times 100, 200 and 300 seconds are given by the slope of the tangents at these times.

Time (s)

Instead of plotting the rate of the reaction versus time, now plot the rate of reaction against the concentration of Br_2

$$\frac{\text{rate}}{[\text{Br}_2]}$$

Note: in this reaction the other reactant (formic acid) is present in large excess, so its concentration does not change much with time.



Plot of rate versus Br₂ concentration. the straight-line relationship shows that the rate of reaction is directly proportional to the Br₂ concentration

[Br₂] (M)

Time (s)	[Br₂] mol/L	Rate (M/s)	Rate (M/s) ————— [Br₂] mol/L
0.0	0.0120	4.20 x 10⁻⁵	3.50 x 10⁻³
50.0	0.0101	3.52 x 10⁻⁵	3.49 x 10⁻³
100.0	0.00846	2.96 x 10⁻⁵	3.50 x 10⁻³
150.0	0.00710	2.49 x 10⁻⁵	3.51 x 10⁻³
200.0	0.00596	2.09 x 10⁻⁵	3.50 x 10⁻³
250.0	0.00500	1.75 x 10⁻⁵	3.50 x 10⁻³
300.0	0.00420	1.48 x 10⁻⁵	3.52 x 10⁻³
350.0	0.00353	1.23 x 10⁻⁵	3.48 x 10⁻³

$$k = \frac{\text{rate}}{[\text{r}_2]}$$

Rate and Concentration

Rate data for the reaction



$[\text{F}_2]$	$[\text{ClO}_2]$	Initial rate
0.10 M	0.010 M	$1.2 \times 10^{-3} \text{ M/s}$
0.10 M	0.040 M	$4.8 \times 10^{-3} \text{ M/s}$
0.20 M	0.010 M	$2.4 \times 10^{-3} \text{ M/s}$



Rate constant

Rate Law

is an expression relating the rate of a reaction to the rate constant and the concentration of the reactants.

determined by experiment

**Exponents in a rate law define
its order.**



First order in F₂

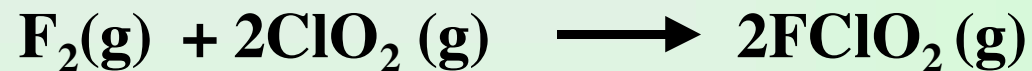
First order in ClO₂

Over all: second order

Exponents in a rate law

$$\text{Rate} = k [\text{F}_2]^1 [\text{ClO}_2]^1$$

have nothing to do with the stoichiometry of the reaction



express the effect of reactant concentration on the rate of reaction

Example



$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	Initial rate (M/s)
0.080	0.034	2.2×10^{-4}
0.080	0.017	1.1×10^{-4}
0.16	0.017	2.2×10^{-4}

Reaction is first order in $\text{S}_2\text{O}_8^{2-}$, first order in I^- second order over all

Example



The order of a reaction must be determined by experiment; it cannot be deduced from overall balanced equation.

order in I⁻ second order over all