Chemical Kinetics

these gases can exist indefinitely at 25°C

$$2H_2(g) + O_2\ (g) \longrightarrow 2H_2O$$

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

$$2C_2H_6(g) \quad + 7O_2\,(g) \longrightarrow 4CO_2\,(g) \;+ 6H_2O$$

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

$\Delta[\text{products}]/\Delta t$ $\qquad$ $d[\text{products}]/dt$

Reactants decrease

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

Reaction of Molecular Bromine and Formic Acid

$$Br_2\,(aq) \quad + \quad \overset{\displaystyle O}{\overset{\|}{HCOH}}\,(aq)$$

$$\downarrow$$

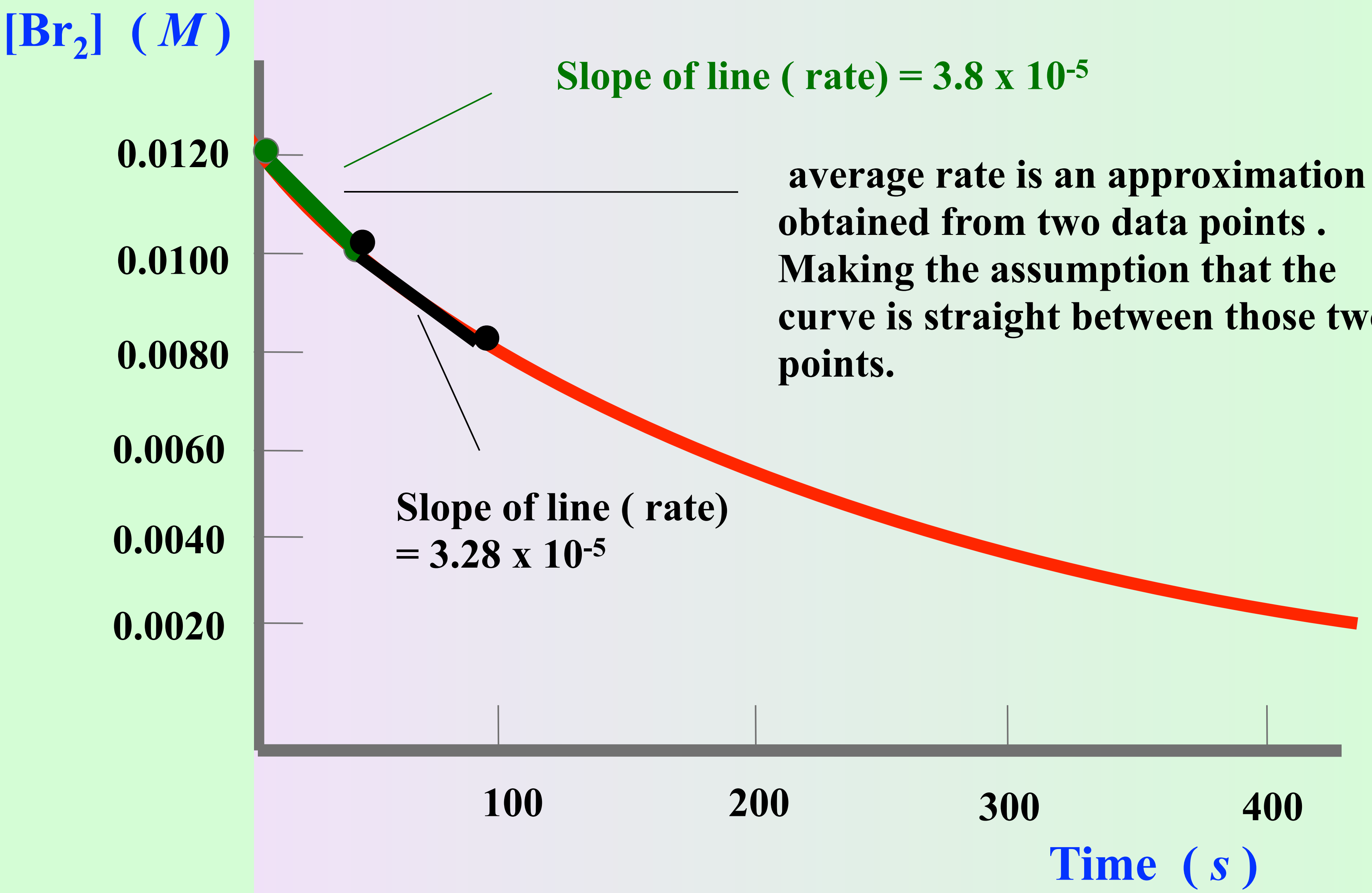
$$2Br^-\,(aq) \;+\; 2H^+(\;aq) \;+\; CO_2(g)$$

How is the rate of a reaction expressed?

Average rate

Time (s)	$[Br_2]$ mol/L	Average Rate (M/s)
0.0	0.0120	
		3.8×10^{-5}
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	

$$-\frac{\Delta[Br_2]}{\Delta t}$$



average rate is an approximation obtained from two data points . Making the assumption that the curve is straight between those two points.

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 x 10^{-5} mol/Ls

$$\begin{array}{c} O \\ \| \\ Br_2\,(aq) + HCOH\,(aq) \longrightarrow \end{array}$$

$$2Br^-\,(aq) + 2H^+(aq) + CO_2(g)$$

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

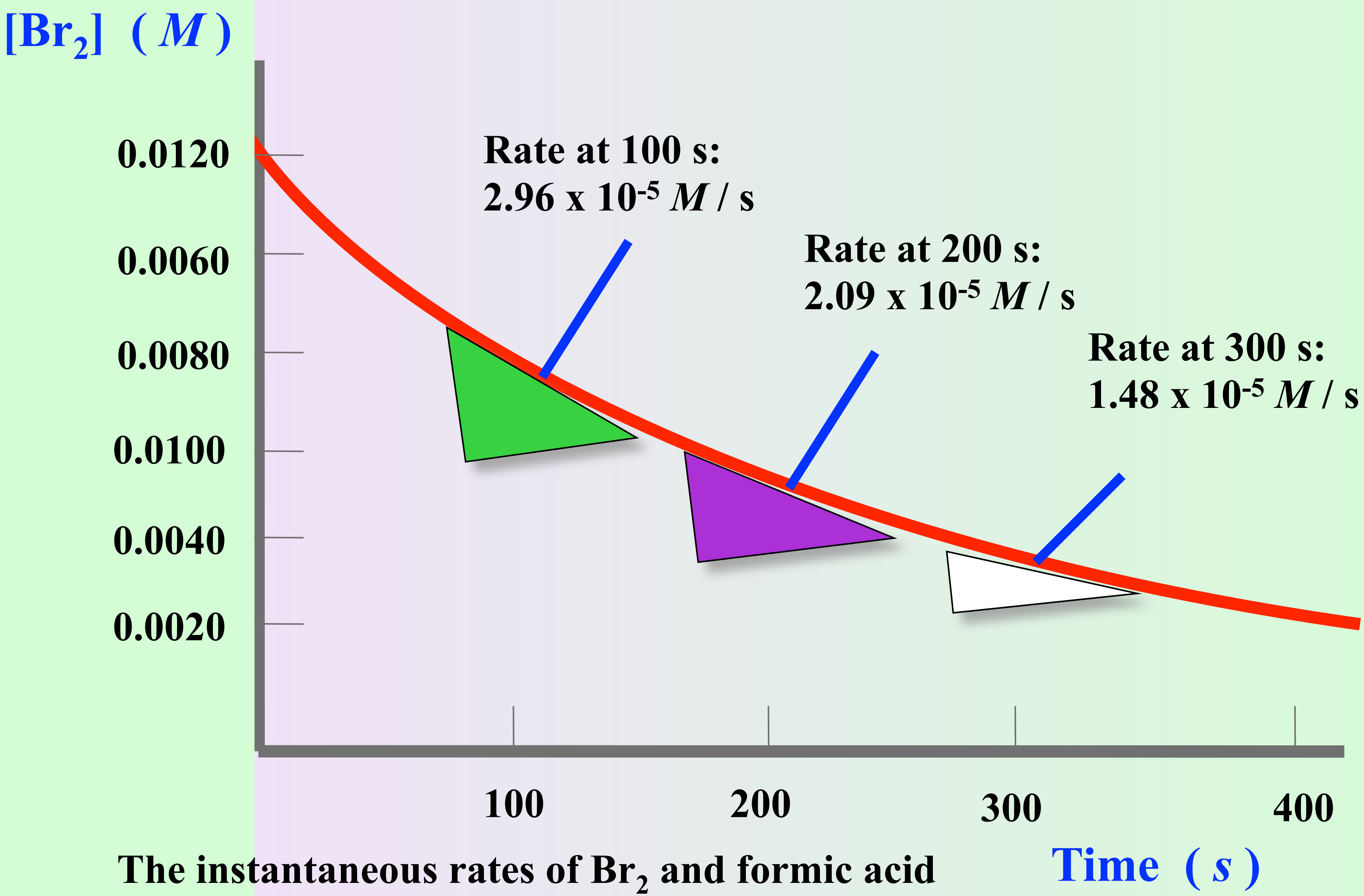
Time (s)	$[Br_2]$ mol/L	Average Rate (M/s)
0.0	0.0120	
		3.8×10^{-5}
50.0	0.0101	
		3.28×10^{-5}
100.0	0.00846	
		2.72×10^{-5}
150.0	0.00710	
		2.28×10^{-5}
200.0	0.00596	
		1.92×10^{-5}
250.0	0.00500	
		1.60×10^{-5}
300.0	0.00420	
		1.34×10^{-5}
350.0	0.00353	

$$-\frac{\Delta[Br_2]}{\Delta t}$$

How is the rate of a reaction expressed?

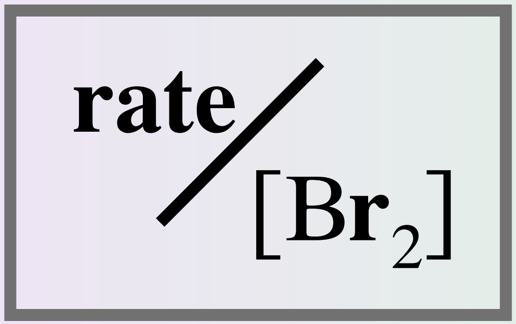
Average rate

Instantaneous rate

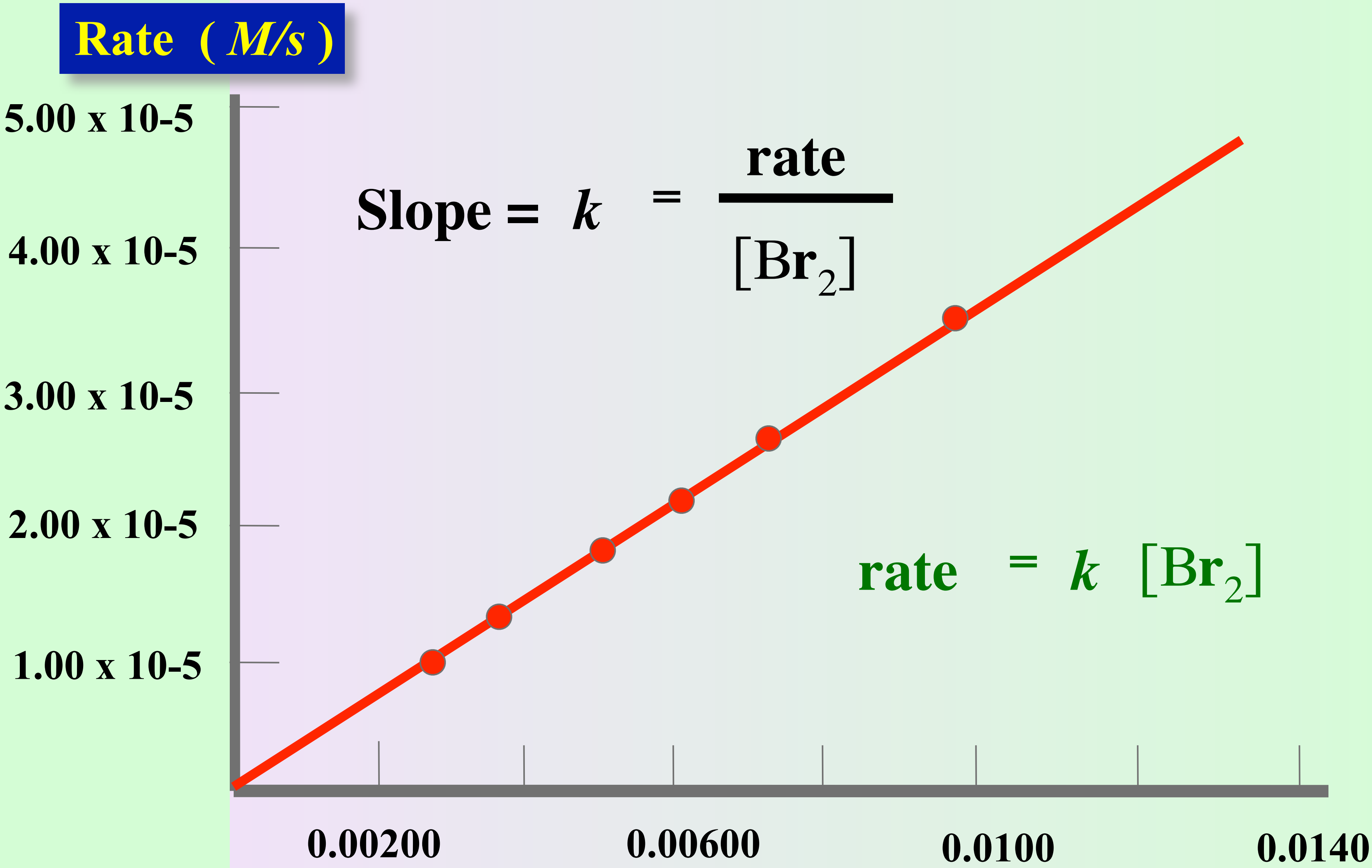


The instantaneous rates of Br_2 and formic acid at times 100,200 and 300 seconds are given by the slope of the tangents at these times.

Instead of plotting the rate of the reaction versus time, now plot the rate of reaction against the concentration of 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 Br_2 concentration. the straight-line relationship shows that the rate of reaction is directly proportional to the Br_2 concentration

Time (s)	$[Br_2]$ mol/L	Rate (M/s)	Rate (M/s) / $[Br_2]$ 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

$$k = \frac{\text{rate}}{[Br_2]}$$

Rate and Concentration

Rate data for the reaction

$$F_2(g) + 2ClO_2(g) \longrightarrow 2FClO_2(g)$$

$[F_2]$	$[ClO_2]$	Initial rate
0.10 M	0.010 M	1.2×10^{-3} M/s
0.10 M	0.040 M	4.8×10^{-3} M/s
0.20 M	0.010 M	2.4×10^{-3} M/s

Rate = k $[F_2]$ $[ClO_2]$

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.

$$\text{Rate} = k\,[F_2]^1[ClO_2]^1$$

First order in F_2

First order in ClO_2

Over all: second order

Exponents in a rate law

$$\text{Rate} = k\,[F_2]^1[ClO_2]^1$$

have nothing to do with the stoichiometry of the reaction

$$F_2(g) + 2ClO_2(g) \longrightarrow 2FClO_2(g)$$

express the effect of reactant concentration on the rate of reaction

Example

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2^-$$

$[S_2O_8^{2-}]$	$[I^-]$	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 $S_2O_8^{2-}$, first order in I^- second order over all

Example

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_3^-$$

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

Reaction is first order in $S_2O_8^{2-}$, first order in I^- second order over all