KINETICS
1: RATE OF REACTION

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KINETICS - INTRODUCTION

Kinetics is the study of rates of reaction (speed of reaction).

- Why we study rates:
  - Speed up reactions.
  - Minimize undesired reactions.
- Useful in drug design.
- Good in understanding how reactions work (e.g. enzymes).

RATE OF REACTION

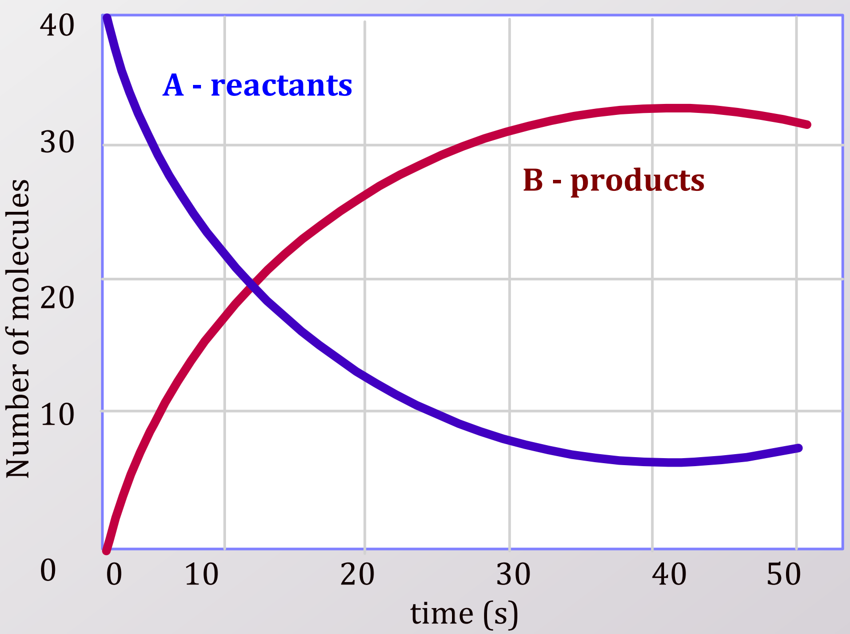
Rate of reaction can be expressed as either disappearance of reactants (negative) or appearance of products (positive).

- For an equation: A $\longrightarrow$ B

  Rate can be: $-\frac{\Delta[A]}{\Delta t}$ *or* $\frac{\Delta[B]}{\Delta t}$

- The negative on A indicates disappearance of products.
- Δ - delta indicates “change”.
- [ ] indicates concentration.

The graph here indicates decrease in molecules of reactants, A, and increase of molecules of product, B, with time.



MONITORING RATE OF REACTION

Rates of reaction can be monitored by the physical changes listed below. For a more quantitative measurement instruments are used.

- Gas evolution (instrument can be used to measure pressure).
- Precipitate formation.
- Color change (visible spectroscopy can be used here).
- Change in pH (pH meter is used to measure this).

In the reaction below, bromine in solution is red colour and thus the reaction can be monitored by the fading of the red colour, as shown in the picture.

$$Br_{2(aq)} + HCOOH_{(aq)} \longrightarrow 2Br^{-}_{(aq)} + 2H^{+}_{(aq)} + CO_{2(g)}$$

AVERAGE RATE

Average rate of reaction is measured by monitoring the change in concentration of reactant or product over time. For the reaction of bromine with formic acid, the concentration of Br_2 is monitored as shown below in the table.

$$Br_{2(aq)} + HCOOH_{(aq)} \longrightarrow 2Br^{-}_{(aq)} + 2H^{+}_{(aq)} + CO_{2(g)}$$

Rates of the Reaction of Molecular Bromine and Formic Acid at 25 °C

Time (s)	$[Br_2]$ (M)	Rate (M/s)
0.0	0.0120	4.20×10^{-5}
50.0	0.0100	3.52×10^{-5}
100.0	0.00846	2.96×10^{-5}
150.0	0.00710	2.49×10^{-5}
200.0	0.00586	2.09×10^{-5}
250.0	0.00500	1.75×10^{-5}
300.0	0.00420	1.48×10^{-5}

The average rate can be calculated the change in concentration

$$\text{Average rate} = \frac{[Br_2]_{\text{final}} - [Br_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

$$\frac{0.0042\ M - 0.0120\ M}{300\ s - 0\ s} = \boxed{2.60 \times 10^{-5} M/s}$$

EXAMPLE 1: AVERAGE RATE

Calculate the average rate of formation of O_2 in a reaction during the time interval from 1200 s to 1800 s. At 1200 s, $[O_2]$ = 0.0036 *M*; at 1800 s, $[O_2]$ = 0.0048 *M*.

Answer:

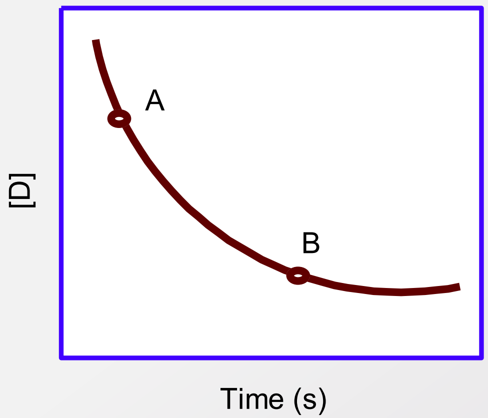
$$\frac{\Delta[O_2]}{\Delta t} = \frac{(0.0048 - 0.0036)\ \mathrm{M}}{(1800 - 1200)\ \mathrm{s}} = \frac{0.0012\ \mathrm{M}}{600\ \mathrm{s}} = \boxed{2.0 \times 10^{-6}\ \mathrm{M/s}}$$

EXAMPLE 2: CONCEPTUAL

Shown here is a plot of the concentration of a reactant D versus time.

a. How do the instantaneous rates at points A and B compare?

b. Is the rate for this reaction constant at all points in time?



Answer:

a. The slope at point A is greater than the slope at point B, so the instantaneous rate at point A is greater than the instantaneous rate at point B.

b. No. If it were, the graph would be linear.

STOICHIOMETRY AND RATE OF REACTION

When stoichiometric ratios are not 1:1 rate of reaction is expressed as follows

General equation:

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t}$$

As indicated "*a*", "*b*" etc. are the stoichiometric coefficients used here. The negative charges show decrease in concentration.

For these calculations it is important to balance the chemical equation

EXAMPLE 3: STOICHIOMETRY AND RATE

Peroxydisulfate ion oxidizes iodide ion to triiodide ion, I_3^-. The reaction is

$$S_2O_8^{2-}{}_{(aq)} + 3I^-{}_{(aq)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + I_3^-{}_{(aq)}$$

How is the rate of reaction that is expressed as the rate of formation of I_3– related to the rate of reaction of I^-?

Answer:

$$\boxed{\frac{\Delta[I_3^-]}{\Delta t} = -\frac{1}{3}\frac{\Delta[I^-]}{\Delta t}}$$

EXAMPLE 4: STOICHIOMETRY AND RATE

For the reaction: $4PH_{3(g)} \longrightarrow P_{4(g)} + 6H_{2(g)}$

If molecular hydrogen is formed at a rate of 0.168 M/s, at what rate is P_4 being produced?

Answer:

$$-\frac{1}{4}\frac{\Delta[\mathrm{PH_3}]}{\Delta t} = \frac{1}{1}\frac{\Delta[\mathrm{P_4}]}{\Delta t} = \frac{1}{6}\frac{\Delta[\mathrm{H_2}]}{\Delta t}$$

$$\frac{1}{6}\frac{\Delta[\mathrm{H_2}]}{\Delta t} = \frac{1}{6}(0.168\mathrm{M/s}) = 0.028\mathrm{M/s}$$

$$\boxed{\frac{1}{1}\frac{\Delta[\mathrm{P_4}]}{\Delta t} = 0.028\mathrm{M/s}}$$

KEY CONCEPTS

- Rate of reaction
- Stoichiometry and rate of reaction