The rate of a reaction

Chemical kinetics: → is the area of chemistry concerned with the speeds or rates at which a chemical reaction occurs.

Kinetic energy: → is the energy available because of the motion of an object.

☒ Kinetics refers to the rate of a reaction

Rate of a reaction: → is the change in the concentration of a reactant or a product with time (M/S).

☒ Any reaction can be represented by the general equation

Reactants →products

☒ This equation tells us that during the course of a reaction:

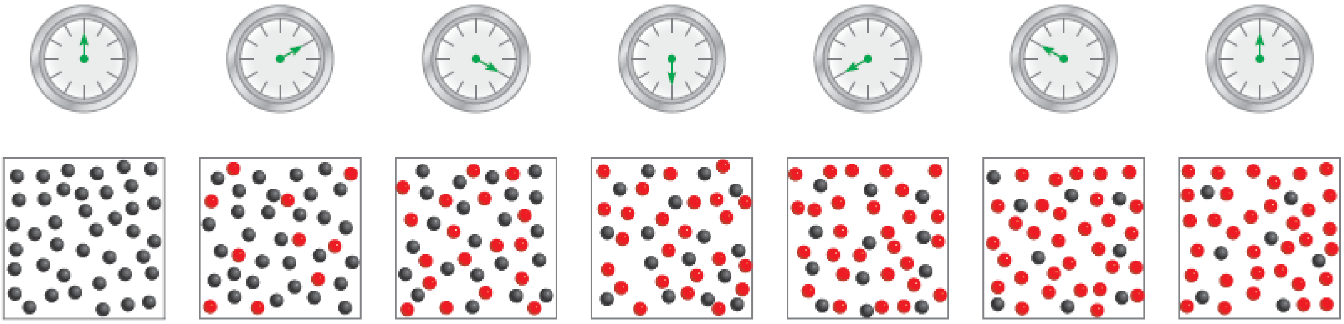
→Reactants are consumed.

→It's concentration decrease.

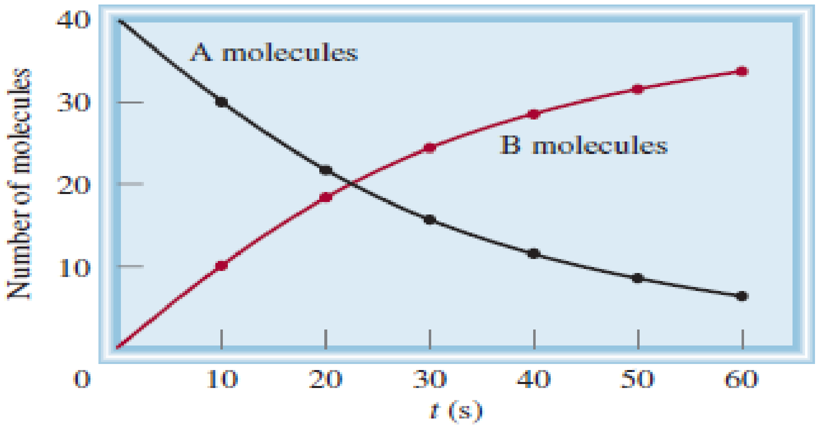
→products are formed.

→It's concentration increase.

☒ This figure shows the progress of a simple reaction in which (A) molecules are converted to (B) molecules..........



☒ The decrease in the number of (A) molecules and the increase in the number of (B) molecules with time are shown in this figure.



For the reaction A→B we can express the rate as

$\text{Rate} = \frac{-\Delta[A]}{\Delta t}$ or $\text{Rate} = \frac{\Delta[B]}{\Delta t}$

Δ[A], Δ[B] :→ change in concentration over a time period.

Δ[A] negative sign :→ refers to the decrease of concentration of (A) with time.

Δ[*B*] positive sign :→ refers to the increase of concentration of (B) with time.

How the rate of a reaction is obtained experimentally?

❖ To determine the rate of a reaction we have to monitor the concentration of the reactant or product as a function of time.

There are three cases to monitor the concentration

For reactions in solution

The concentration can often be measured by spectroscopic means.

Reactions involving ions

The concentration can also be detected by electrical conductance measurement.

Reactions involving gases

The concentration can be measured by pressure measurements.

☒ Two specific reactions for which different methods are used to measure the reaction rates.

(1)Reaction of molecular bromine and formic acid.

$$Br_2 + HCOOH \rightarrow 2Br^-_{(aq)} + 2H^+_{(aq)} + CO_{2(g)}$$

Note that

- Br_2 is reddish brown in color
- All of the other species in the reaction colorless.
- As the reaction progresses, the concentration of Br_2 steadily decreases and its color fades.

- This loss of color and hence concentration can be monitored by spectrometer.

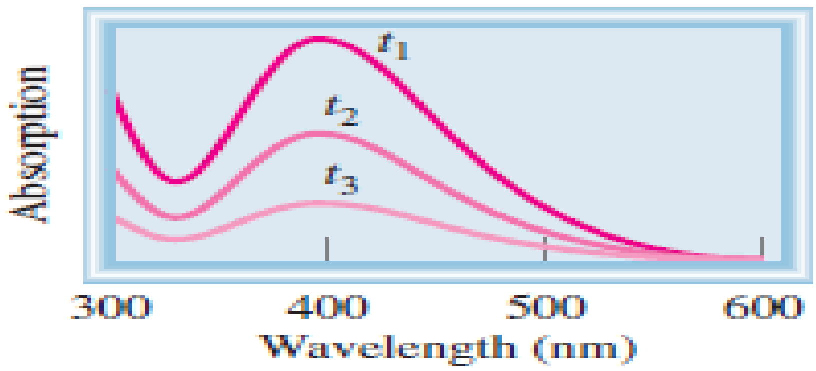


Figure show: Plot of absorption of bromine versus wavelength. The maximum absorption of visible light by bromine occurs at 393 nm. As the reaction progresses (t_1 to t_3), the absorption, which is proportional to $[Br_2]$, decreases.

- Measuring the decrease in bromine concentration at same initial time and then at same final time enables us to determine the average rate of the reaction.

$$\text{Average rate} = \frac{-\Delta[Br_2]}{\Delta t} = \frac{-[Br_2]final - [Br]2\ intial}{tfinal - tinitial}$$

- Using the data provided in this table we can calculate the average rate over the first 50-S time interval as follows:

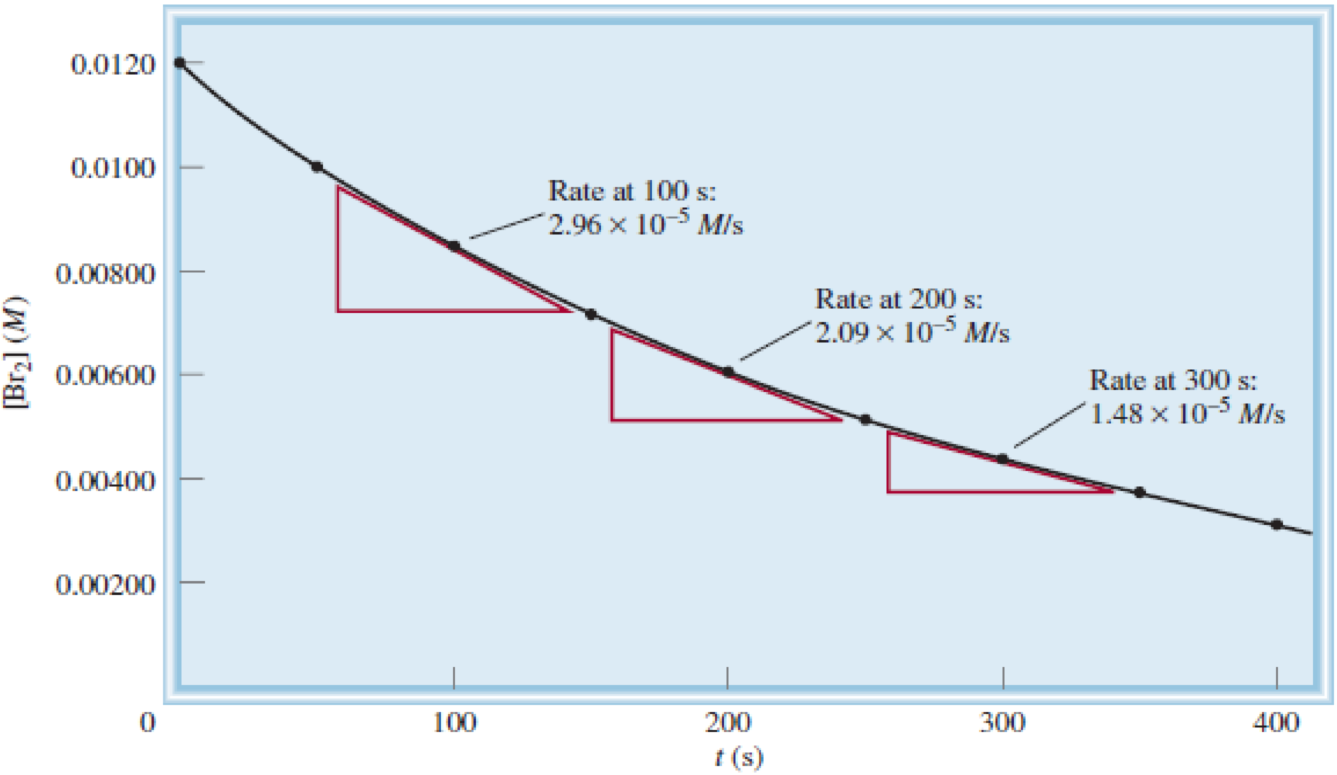
Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

$$\text{Average rate} = \frac{-[Br_2]f - [Br_2]i}{tfinal - tinitial} = \frac{-[0.0101 - 0.0120]}{50\ s} M = 3.8 * 10^{-5}\ M/s$$

- If we had chosen the first 100 S as our time interval.

$$\text{Average rate} = \frac{-[0.00846 - 0.0120]}{100s} M = 3.54 * 10^{-5}\ M/S$$

- The average rate of the reaction depends on the time interval we choose.
- This figure show plots of $[Br_2]$ versus time based



Note that

- Graphically, the instantaneous rate at 100 S after the start of the reaction is given by the slope of the tangent to the curve at that instant.
- The instantaneous rate at any other time can be determined in a similar manner.
- The instantaneous rate determined in this way will always have the same value for the same concentration of reactants, as long as the temperature is kept constant.
- Rate of the bromine- formic acid reaction also depend on the concentration of formic acid, however, by adding a large excess of formic acid to reaction mixture, concentration of formic acid remains constant.
- Under this condition the change in the amount of formic acid present in solution has no effect on the measured rate.

The effect that the bromine concentration has on the rate of reaction

From above table we see that:

- As the concentration of bromine is doubled, the rate of reaction also doubles.

Thus: the rate is directly proportional to the $[Br_2]$ concentration

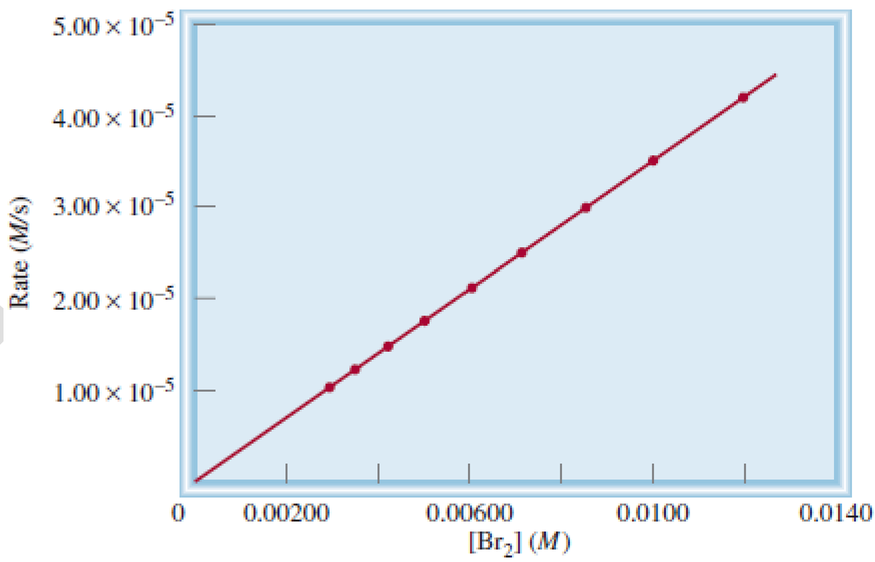
Rate $\propto [Br_2]$ K$\longrightarrow$ rate constant

$= K[Br_2]$

Rate constant: $\rightarrow$ a constant of proportionality between the reaction rate and the concentration of reactant.

- This direct proportionality between $[Br_2]$ concentration and rate is also supported by plotting the data.

Plot of the rate versus $[Br_2]$concentration



Note that

- The fact that this graph is a straight line shows that the rate is directly proportional to the concentration.
- The higher the concentration, the higher the rate.

From the last equation

$$K = rate/[Br_2]$$

The unit of rate → M/S   the unit of K = $\frac{\cancel{M}}{S*\cancel{M}}$ = 1/S or S^{-1}

The unit of $[Br_2]$ → M

Note that

- K is constant for every reaction and not affected by the concentration of $[Br_2]$but depends on temperature.
- The rate is greater at a higher concentration and smaller at a lower concentration of $[Br_2]$.

(2) Decomposition of hydrogen peroxide

- If one of the products or reactants is a gas, we can use a manometer to find the reaction rate.
- Consider the decomposition of hydrogen peroxide at 20°C.

$$2H_2O_{2\,(aq)} \rightarrow 2H_2O_{(L)} + O_{2(g)}$$

- The rate of decomposition can be determined by monitoring the rate of oxygen evolution with a manometer.
- The oxygen pressure can be readily converted to concentration.

☒ By using the ideal gas equation

$$PV = nRT$$

$$P = \frac{n}{V}RT = [O_2]RT$$

$(\frac{n}{V})$ →Molarity of oxygen gas.

Rearranging the equation

$$[O_2] = \left(\frac{1}{RT}\right)P$$

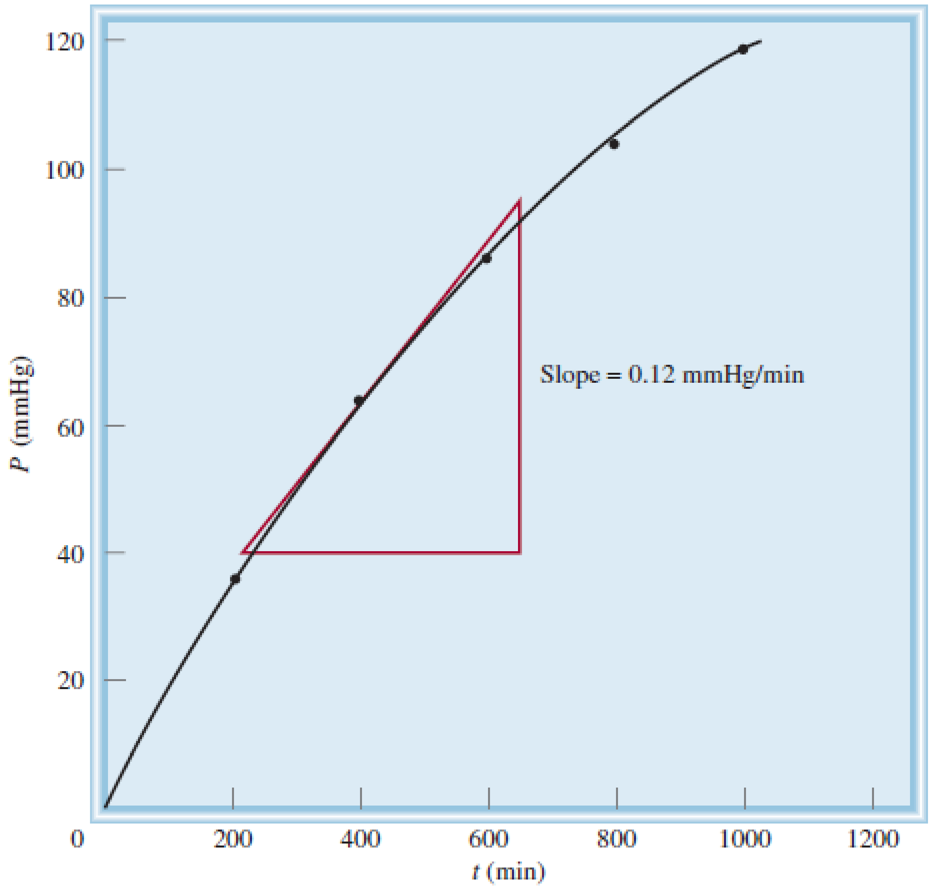


Figure show: The instantaneous rate for the decomposition of hydrogen peroxide at 400 min is given by the slope of the tangent multiplied by 1/RT. The reaction rate " rate of oxygen production"

☒ Reaction rates and stoichiometry

For stoichiometrically simple reaction of the type

$$A \rightarrow B$$

- The rate can be expressed as → the decrease in reactant concentration with time $\frac{-\Delta[A]}{\Delta t}$.
- The increase in product concentration with time = $\frac{\Delta[B]}{\Delta t}$.
- For more complex reactions: →we must be careful in writing the rate expression.

Consider, for example

$$2A \rightarrow B$$

- Two moles of (A) disappear for each mole of (B) that forms.

That is

- The rate at which (B) forms is one-half the rate at which (A) disappears.

$$\text{Rate} = -\frac{1}{2}\left(\frac{\Delta[A]}{\Delta t}\right) \quad \text{or} \quad \text{rate } \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction

$$aA + bB \rightarrow cC + dD$$

The rate is given by = $\left(\frac{-1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{-1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right) = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\ \frac{\Delta[D]}{\Delta t}$

Example

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

(a) $I_{2(aq)} + OCl_{2(aq)} = Cl_{2(aq)} + OI_{2(aq)}$

(b) $4NH_{3(g)} + 5O_{2(g)} = 4NO_{(g)} + 6H_2O_{(g)}$

Solution

(a) Because each of the stoichiometric coefficients equals 1,

$$\text{Rate} = -\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[OCl^-]}{\Delta t} = \frac{\Delta[Cl^-]}{\Delta t} = \frac{\Delta[OI^-]}{\Delta t}$$

(b) Here the coefficients are 4, 5, 4, and 6, so

$$\text{Rate} = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Choose

1) ……… is the area of chemistry concerned with the speeds or rates at which a chemical reaction occurs.

A) Chemical Kinetics
B) Rate of reaction
C) Chemical reaction
D) Mechanical chemistry

2) ……… is the change in the concentration of a reactant or a product with time.

A) Chemical Kinetics
B) Rate of reaction
C) Chemical reaction
D) Mechanical chemistry

3) During the course at a reaction, reactants concentration…… while product concentration…….

A) Increase-increase
B) Increase-decrease
C) decrease-increase
D) decrease-decrease

4) For the reaction "A→B" we can express the rate as…….

A) $-\frac{dA}{dt}$
B) $\frac{dA}{dt}$
C) $\frac{-dB}{dt}$
D) Both A and C

5) For the reaction " X→Y " we can express the rate as…….

A) $\frac{dy}{dt}$

C) $\frac{-dx}{dt}$

B) $\frac{-dy}{dt}$

D) Both A and C

6) The unit of rate is………

A) M/S

C) M.S

B) L/S

D) none of them

7) The energy available because of the motion of an object is…….

A) Kinetic energy

C) solar energy

B) Potential energy

D) Heat capacity

8) Rate of reaction is …….. Quantity.

A) positive

B) negative

9) The units of "reaction rate" are………….. .

A) L mol^{-1} s^{-1}

C) mol L^{-1} s^{-1}.

B) L^2 mol^{-2} s^{-1}.

D) s^{-2}.

10) For the reaction $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$ at a particular time, $-\Delta[BrO_3^-]/\Delta t = 1.5 \times 10^{-2}$ M/s. What is $-\Delta[Br^-]/\Delta t$ at the same instant?

A) 13 M/s
B) 7.5×10^{-2} M/s
C) 1.5×10^{-2} M/s
D) 3.0×10^{-3} M/s

11) For the following reaction, $\Delta P(C_6H_{14})/\Delta t$ was found to be -6.2×10^{-3} atm/s.

$$C_6H_{14}(g) \rightarrow C_6H_6(g) + 4H_2(g)$$

Determine $\Delta P(H_2)/\Delta t$ for this reaction at the same time.

A) 6.2×10^{-3} atm/s
B) 1.6×10^{-3} atm/s
C) 2.5×10^{-2} atm/s
D) -1.6×10^{-3} atm/s

12) For the reaction $C_6H_{14}(g) \rightarrow C_6H_6(g) + 4H_2(g)$, $\Delta P(H_2)/\Delta t$ was found to be 2.5×10^{-2} atm/s, where $\Delta P(H_2)$ is the change in pressure of hydrogen. Determine $\Delta P(C_6H_{14})/\Delta t$ for this reaction at the same time.

A) 2.5×10^{-2} atm/s
B) -6.2×10^{-3} atm/s
C) -2.5×10^{-2} atm/s
D) 0.10 atm/s