Biophysical chemistry

Part A
Chapter: 3
Chemical kinetics
Lecture - 1

Fahmida Akter Lia
Department of Biochemistry
National Institute of Science and Technology(NIST)

Chemical kinetics

“kinetic” - movement or change
-the area of chemistry concerned with the speeds, or rates, at which a chemical reaction occurs.

the rate of a reaction, or the reaction rate: -the change in the concentration of a reactant or a product with time (M/s).

why study the rate of a reaction?

- intrinsic curiosity - initial steps in vision and photosynthesis and nuclear chain reactions - $10^{-12}s$ to $10^{-26}s$

  conversion of graphite to diamond - years or millions of years to complete.
- useful in drug design,
- in pollution control, and in food processing.

The Rate of a Reaction

the general equation

↓ reactants ⟶ products ↑

we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Ex: A molecules are converted to B molecules:

$$A \longrightarrow B$$

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

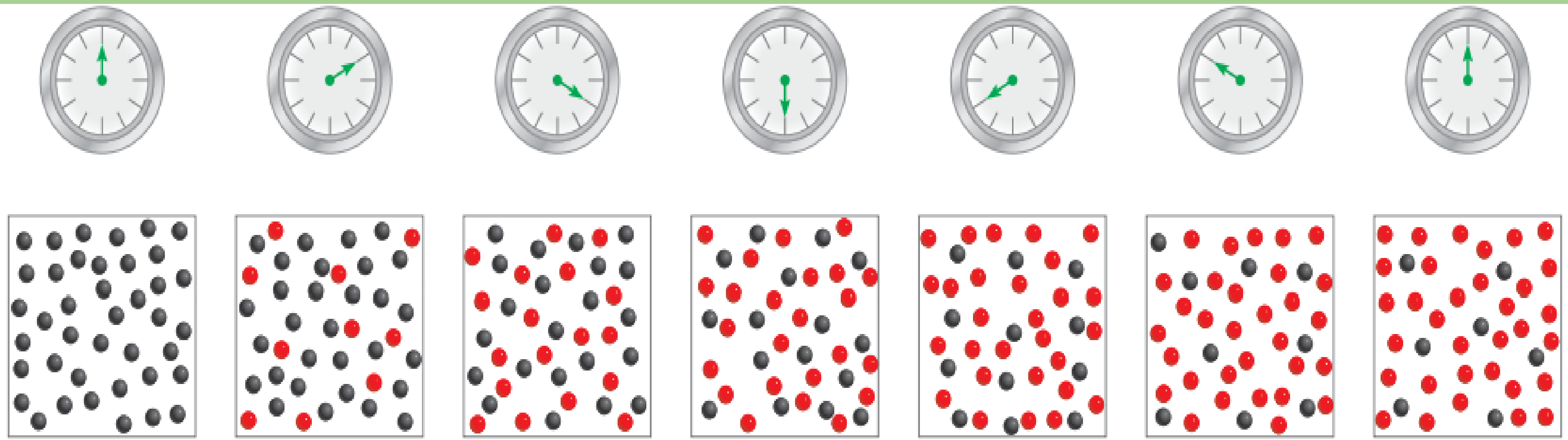
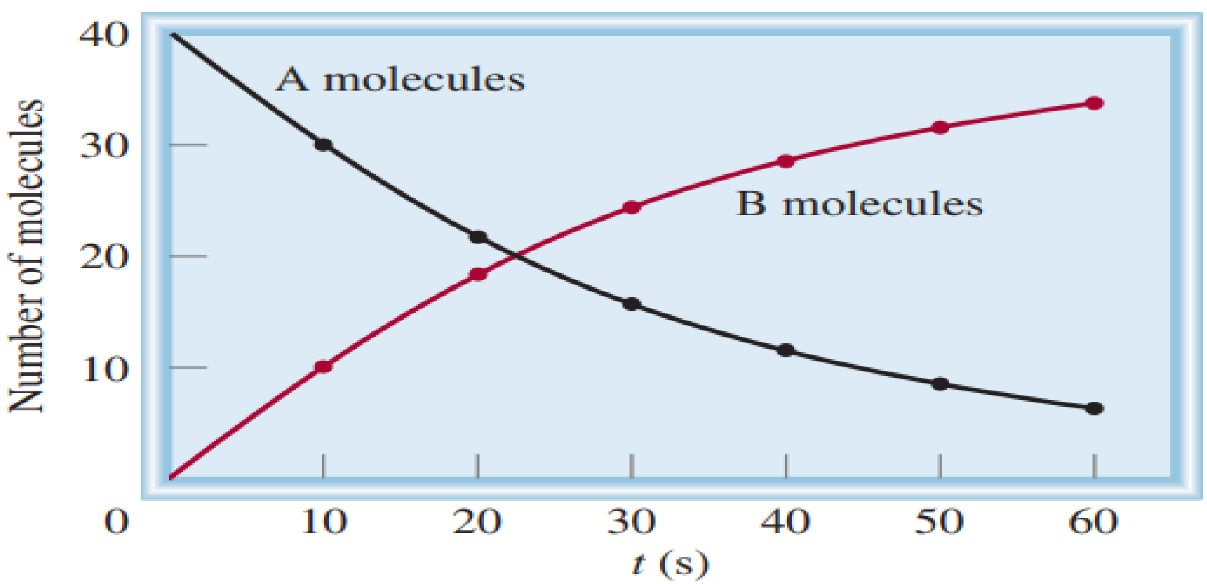


Figure 13.1 *The progress of reaction A ⟶ B at 10-s intervals over a period of 60 s. Initially, only A molecules (gray spheres) are present. As time progresses, B molecules (red spheres) are formed.*



These rates are average rates because they are averaged over a certain time period Δt.

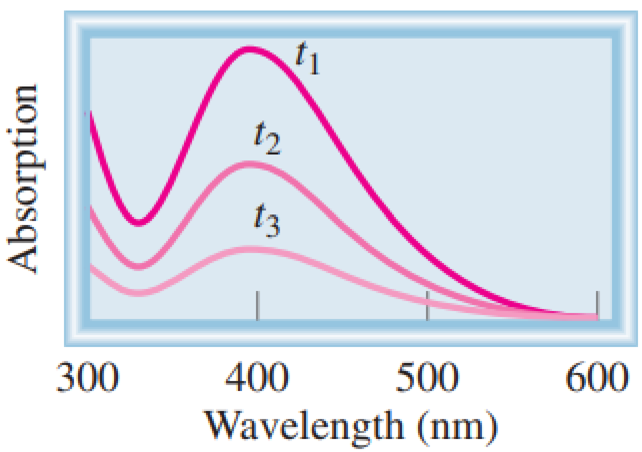
The Rate of a Reaction

❖ Reaction of Molecular Bromine and Formic Acid

In aqueous solutions, molecular bromine reacts with formic acid (HCOOH) as follows:

$$Br_2(aq) + HCOOH(aq) \longrightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

Figure 13.3 *From left to right: The decrease in bromine concentration as time elapses shows up as a loss of color (from left to right).*



The Rate of a Reaction

❖ Reaction of Molecular Bromine and Formic Acid

$$\text{average rate} = -\frac{\Delta[Br_2]}{\Delta t}$$

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

TABLE 13.1 Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

Time (s)	$[Br_2]$ (*M*)
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
400.0	0.00296

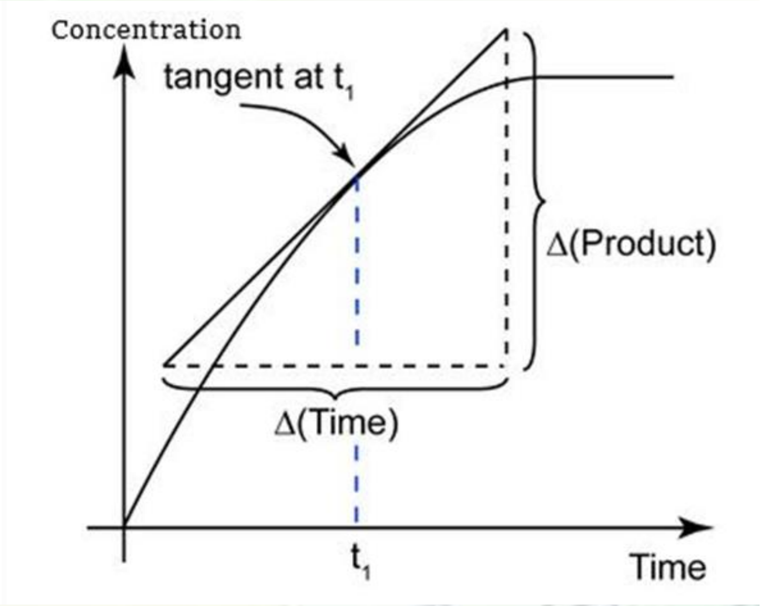
$$\text{average rate} = -\frac{(0.0101 - 0.0120)M}{50.0\ s} = 3.80\times10^{-5}\ \text{M/S}$$

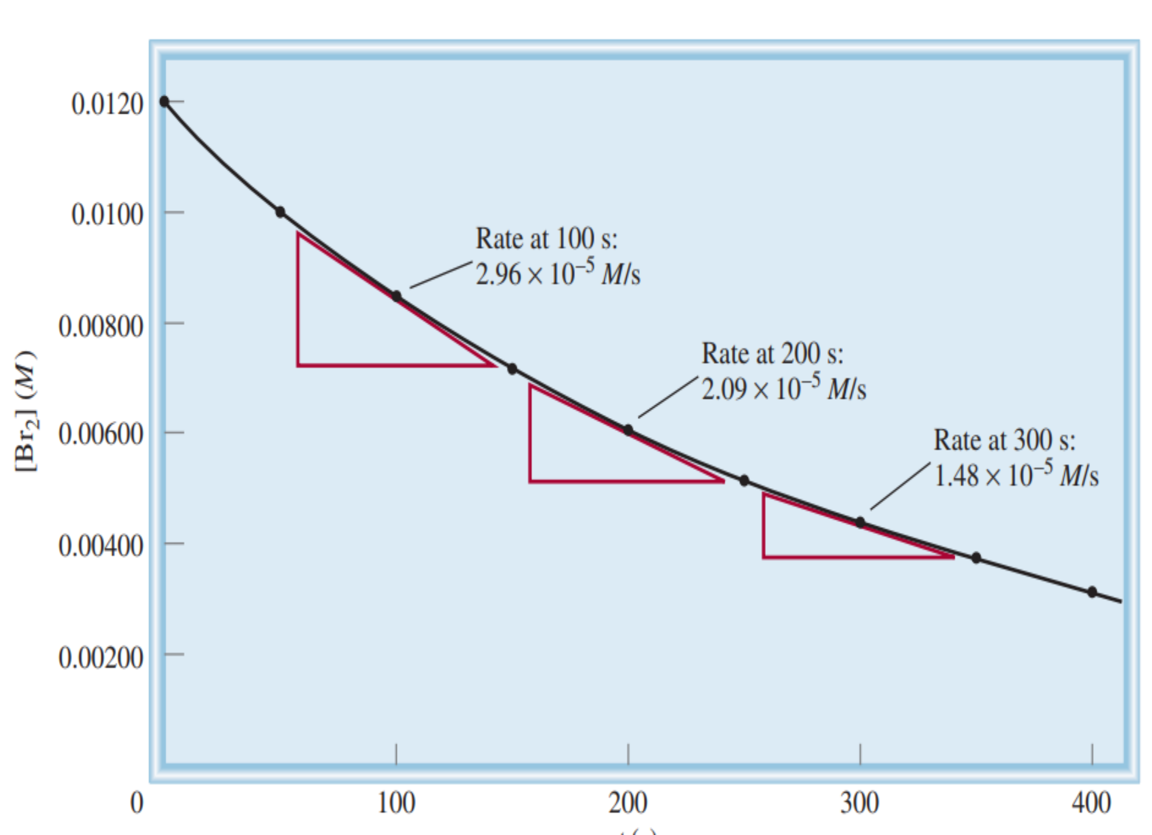
$$\text{average rate} = -\frac{(0.00846 - 0.0120)M}{100.0\ s} = 3.54\times10^{-5}\ \text{M/S}$$

the average rate of the reaction depends on the time interval we choose

The Rate of a Reaction

By calculating the average reaction rate over shorter and shorter intervals, we can obtain the rate for a specific instant in time - instantaneous rate of the reaction at that time.





The Rate of a Reaction

TABLE 13.1 Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

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}

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

k, the rate constant = a constant of proportionality between the reaction rate and the concentration of reactant.

the unit of k is 1/s, or s^{-1} in this case.

as the concentration of bromine is doubled, the rate of reaction also doubles. Thus, the rate is directly proportional to the Br2 concentration,

The rate also depends on [formic acid]. However, by adding a large excess of formic acid to the reaction mixture we can ensure that the concentration of formic acid remains virtually constant throughout the course of the reaction. Under this condition the change in the amount of formic acid present in solution has no effect on the measured rate