KINETICS -1
RATE OF REACTION

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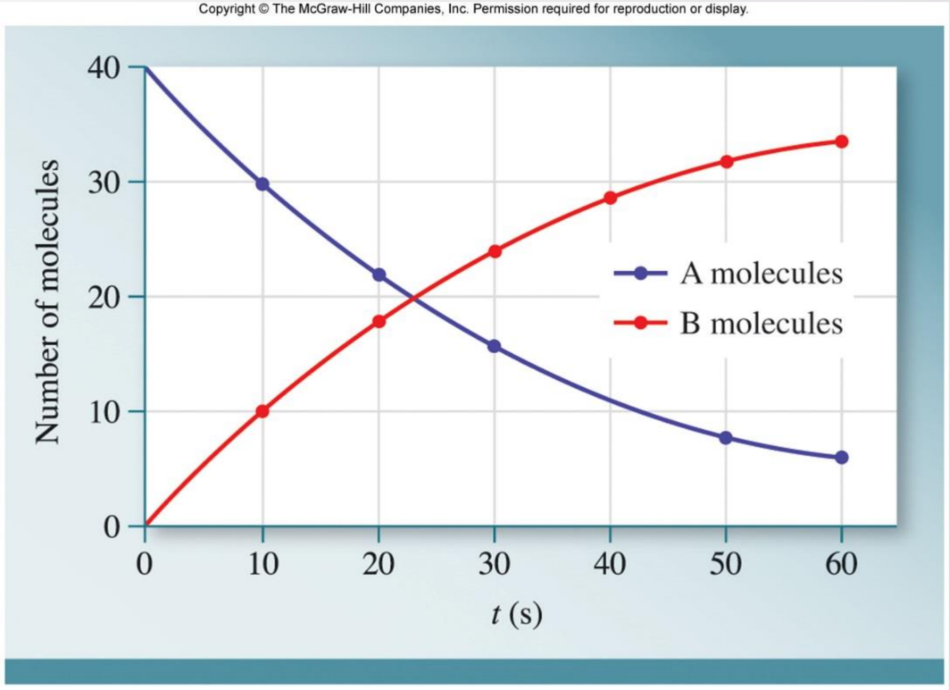
KINETICS - INTRODUCTION

- 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 -> B
- Rate can be: $-\frac{\Delta [A]}{\Delta t}$ *or* $\frac{\Delta [B]}{\Delta t}$
- The negative on A indicates disappearance of products.
- Δ indicates "change"



MONITORING RATE OF REACTION

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

Note: Br_2 disappears over time

- Rates of reaction can be monitored by:
    - Gas evolution
    - Precipitate formation
    - Color change
    - Change in pH etc.

AVERAGE RATE

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

TABLE 14.1	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	0.0101	3.52×10^{-5}
100.0	0.00846	2.96×10^{-5}
150.0	0.00710	2.49×10^{-5}
200.0	0.00596	2.09×10^{-5}
250.0	0.00500	1.75×10^{-5}
300.0	0.00420	1.48×10^{-5}
350.0	0.00353	1.23×10^{-5}
400.0	0.00296	1.04×10^{-5}

$$\text{Average rate} = \frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}} = \frac{0.0101\,M - 0.0120\,M}{50\,s - 0\,s} = 3.80 \times 10^{-5}\ M/s$$

EXAMPLE: AVERAGE RATE

Calculate the average rate of formation of O_2 in the following 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*.

Solution:

$$\frac{\Delta[O_2]}{\Delta t} = \frac{(0.0048 - 0.0036)\,M}{(1800 - 1200)\,s}$$

$$= \frac{0.0012\,M}{600\,s}$$

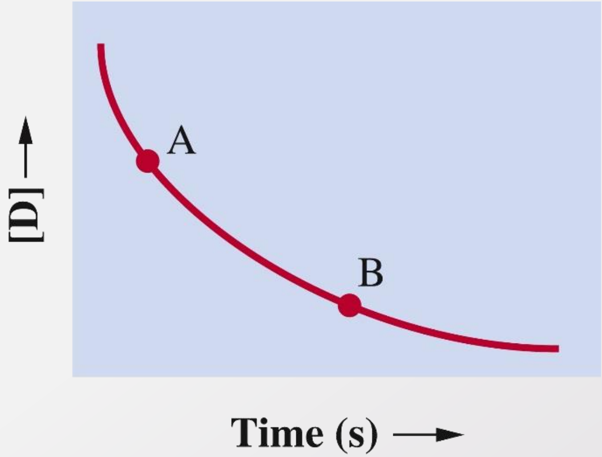
$$= 2.0 \times 10^{-6}\,M/s$$

EXAMPLE: 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?



Solution:

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:

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

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

Problem:

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

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

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^-?

Solution:

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

EXAMPLE: STOICHIOMETRY AND RATE

For the reaction: $4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$

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

Solution:

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

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

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

KEY CONCEPTS

- Rate of reaction
- Stoichiometry and rate of reaction