Grade 12 Chemistry

Energy Changes and Rates of Reaction

Class 9

Chemical Kinetics

- In chemical kinetics, we ask

  "How fast does the reaction go?"

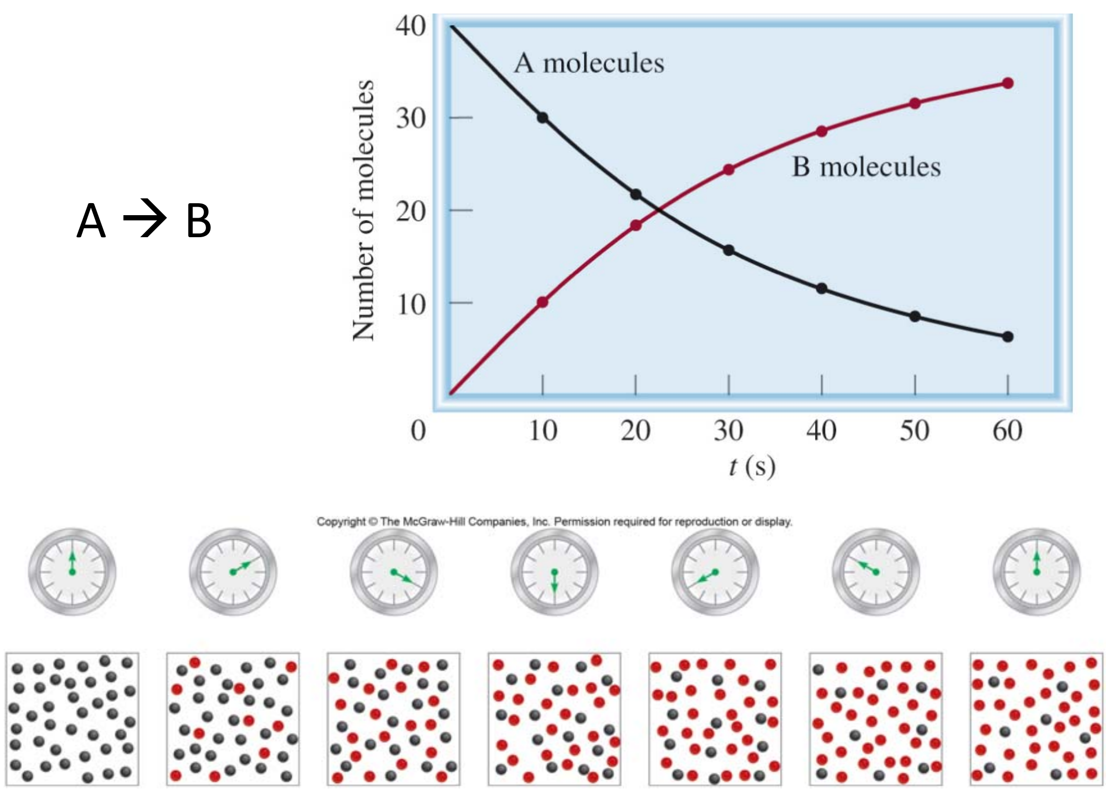
- **Chemical Kinetics:** the speed or rate at which chemical reactions occur

Reaction Rates

Rate = $\frac{\text{Concentration change}}{\text{Time change}}$

- Reaction rate is the change in the concentration of a reactant or product with time
- Units = mol/(L•s) or M/s
- Reactions rates are always positive by convention; rate of product increasing or reactant decreasing

A → B



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

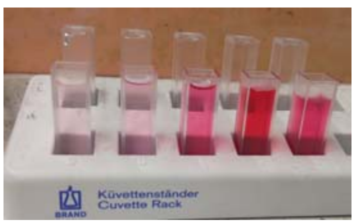
$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

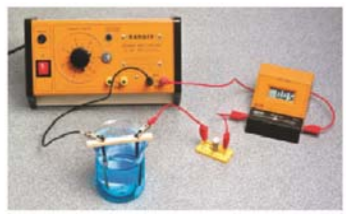
These rates are average rates because they are averaged over a certain time period.

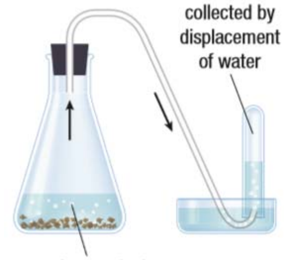
How do we obtain rate of reaction?

- Experiments monitor the concentration of the reactant (or product) with time
  - **Solution:** concentration is measured by spectrophotometer due to colour differences
  - **Ions:** concentration measured by electrical conductance measurements
  - **Gases:** concentration measured by pressure measurements

Solution	Ions	Gases
• Colour changes • pH changes	• Conductivity using a conductivity meter	• Changes in pressure • Amount of gas produced • Amount of water displaced • Change in mass







Average Rate of Reaction

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

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

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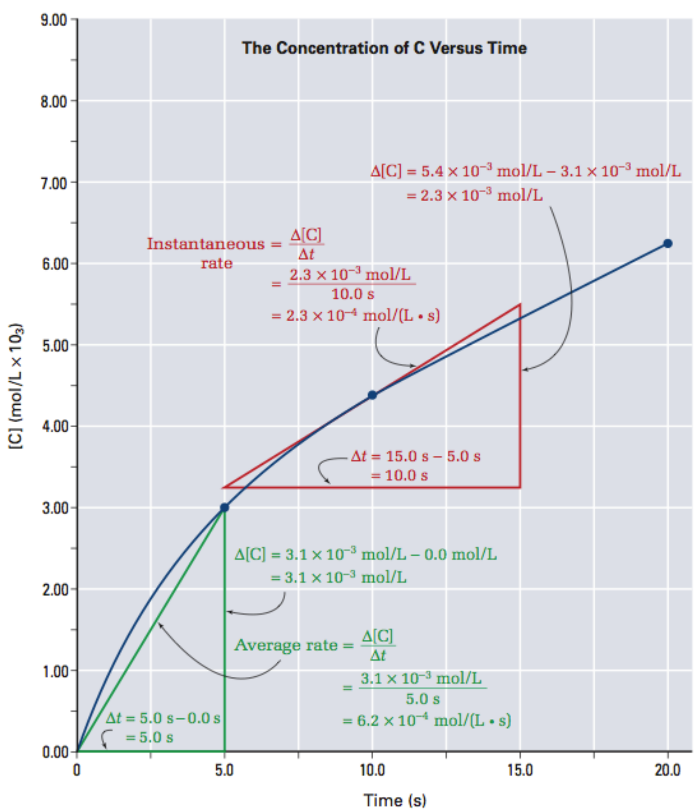
TABLE 13.1	Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C		
Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	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}

$$\text{average rate} = -\frac{(0.0101 - 0.0120)\text{M}}{50.0\text{s}} = 3.80 \times 10^{-5}\,\text{M/s}$$



Average rate of a reaction is represented by the slope of a line that is drawn between two points on the curve = **secant**

Checkpoint

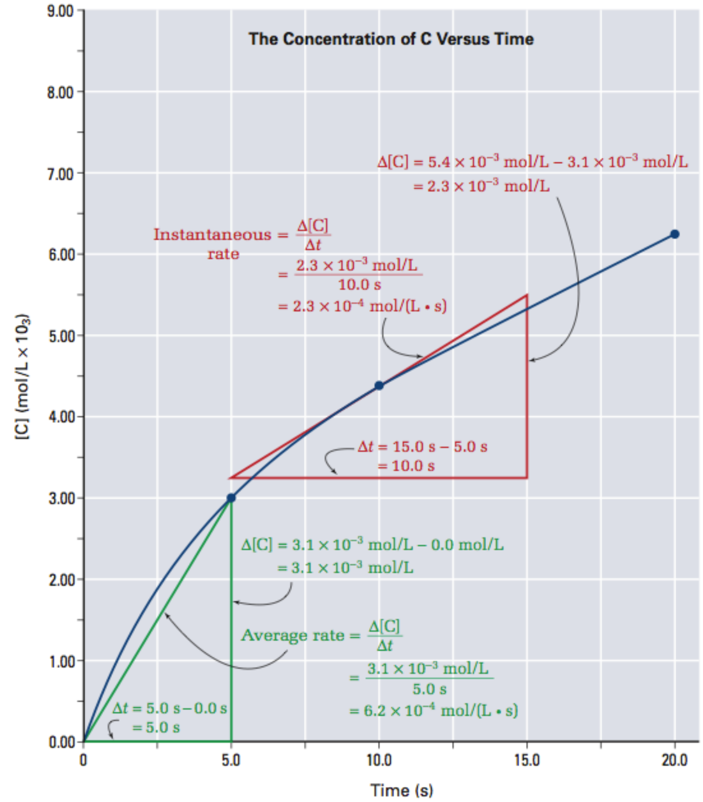
Determine the average rate of the reaction from t = 0.0 s to t = 5.0 s.

Table 6.1 Concentration of C During a Reaction at Constant Temperature

Time (s)	[C] (mol/L)
0.0	0.00
5.0	3.12×10^{-3}
10.0	4.41×10^{-3}
15.0	5.40×10^{-3}
20.0	6.24×10^{-3}

Instantaneous Rate of Reaction

- By calculating the average reaction rate over shorter and shorter intervals, we obtain the rate for a specific instant in time
- Instantaneous rate is the rate of reaction at a certain point in time
- Instantaneous rate = slope of the **tangent** (line that touches the curve at one point)
- Instantaneous rate at t = 0 is the **initial rate**



Instantaneous rate of a reaction is represented by the slope of a line drawn to the curve = **tangent**

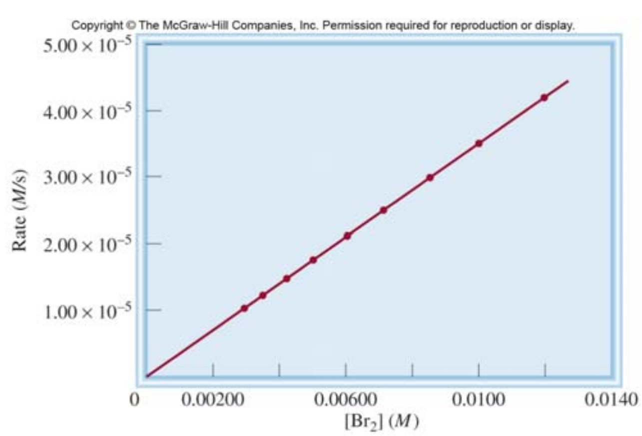
Rate Constant (*k*)

- If we plot a rate versus concentration graph, we obtain a straight line-relationship

$$\text{rate} \propto [\mathrm{Br_2}]$$

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

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



- **Rate Constant (*k*)** is a constant of proportionality between the reaction rate and the concentration of reactant

- Using the Data on Table 13.1, at t = 50 s

$$k = \frac{\text{rate}}{[\mathrm{Br_2}]} = \frac{3.52 \times 10^{-5}\,\mathrm{M/s}}{0.0101\mathrm{M}} = 3.49 \times 10^{-3}\,\mathrm{s}^{-1}$$

- The magnitude of *k*, indicates the speed of the reaction:
  - Small *k* = slow reaction (10^{-3} s^{-1} = 2 hours)
  - Large *k* = fast reaction (10^{2} s^{-1} = 0.10 sec)

- The value of *k* remains constant under constant conditions; does not depend on the concentration of the reactants since the ratio of rate/[Br_2] remains the same under constant temperature
  - *k* changes with changing temperature

Reaction Rates and Stoichiometry

2A → B

$$\text{rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

*a*A + *b*B → *c*C + *d*D

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

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

- For every O_2 that is produced, 4 moles of NO_2 is produced and 2 moles of N_2O_5 disappears
- Therefore:

$$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\left[\frac{\Delta[NO_2]}{\Delta t}\right] = -\frac{1}{2}\left[\frac{\Delta[N_2O_5]}{\Delta t}\right]$$

Checkpoint

Given: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

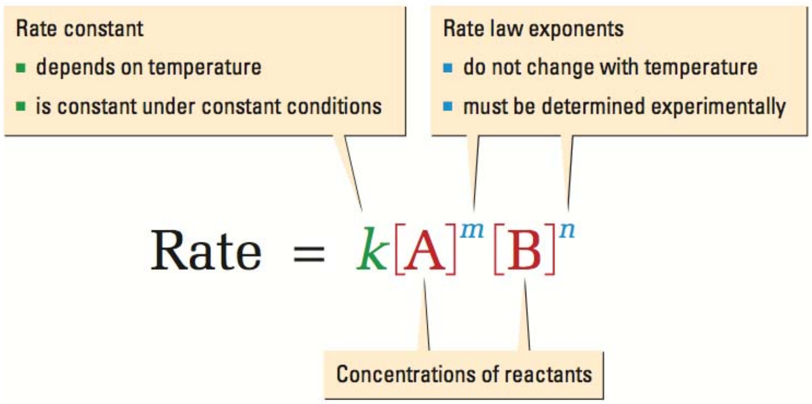
If NO_2 is produced at a rate of 5.0×10^{-6} mol/L•s what is the corresponding rate of disappearance of N_2O_5 and the formation of O_2?

Factors Affecting Reaction Rate

- The rate of a reaction can be increased by increasing the temperature
- Increasing the concentration of the reactants usually increases the rate of the reaction
- A catalyst is a substance that increases the rate of the reaction
- Increasing the available surface area of a reactant increases the rate of reaction
- The rate of a chemical reactions depends on what the reactants are

The Rate Law

- The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentration of the reactants raised to some powers



$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

$$\text{Rate} = k[\mathrm{A}]^m[\mathrm{B}]^n$$

Where:

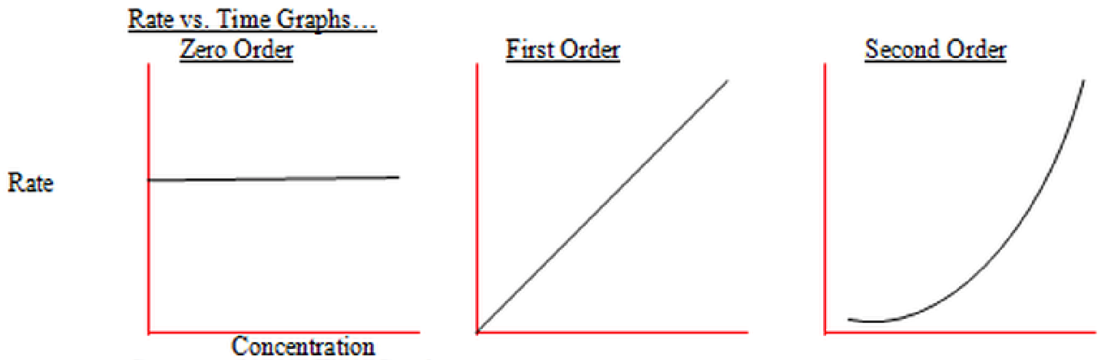
m = the order of the reaction with respect to A

n = the order of the reaction with respect to B

k = rate constant

(m+n) = the overall order of the reaction

*Rate law can only be determined experimentally



- Exponent of 0 = 0^{th} order
  - Rate is independent of the concentration of the reactant present
- Exponent of 1 = 1^{st} order
- Exponent of 2 = 2^{nd} order

Checkpoint

If Rate = $k[A]^2[B]$, what is the order of A, B and the overall reaction?

Experimental Determination of the Rate Law

- Chemists find the rate law by conducting a series of experiments with different initial concentrations
  - All other factors (i.e. temperature) remain constant
- Ex: $2N_2O_5(g) \rightarrow 2NO_2(g) + O_2(g)$ Rate = $k[N_2O_5]^m$

Table 6.2 Data for Rate Experiments

Experiment	Initial $[N_2O_5]_0$ (mol/L)	Initial rate (mol/(L • s))
1	0.010	4.8×10^{-6}
2	0.020	9.6×10^{-6}
3	0.030	1.5×10^{-5}

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Rate = $k[N_2O_5]^m$

Create a ratio to compare the two rates.

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k(0.010\ \text{mol/L})^m}{k(0.020\ \text{mol/L})^m} = \frac{4.8 \times 10^{-6}\ \text{mol/(L • s)}}{9.6 \times 10^{-6}\ \text{mol/(L • s)}}$$

Since k is a constant for reactions that occur at a constant temperature, you can cancel out k.

$$\frac{\cancel{k}(0.010\ \cancel{\text{mol/}}\text{L})^m}{\cancel{k}(0.020\ \cancel{\text{mol/}}\text{L})^m} = \frac{4.8 \times 10^{-6}\ \cancel{\text{mol/}}(\text{L • s})}{9.6 \times 10^{-6}\ \cancel{\text{mol/}}(\text{L • s})}$$

$$(0.5)^m = 0.5$$

$$m = 1 \text{ (by inspection)}$$

- Once you know the rate law equation, you calculate the rate constant using the results from the experiment

Rate = $k[N_2O_5]^1$

$$4.8 \times 10^{-6}\ \text{mol/(L} \bullet \text{s)} = k(0.010\ \text{mol/L})$$

$$k = \frac{4.8 \times 10^{-6}\ \cancel{\text{mol/}}\text{(L} \bullet \text{s)}}{0.010\ \cancel{\text{mol/L}}}$$

$$= 4.8 \times 10^{-4}\ \text{s}^{-1}$$

STOP Checkpoint STOP

When heated, ethylene oxide decomposes to produce methane and carbon monoxide.

$C_2H_4O_{(g)} \rightarrow CH_{4(g)} + CO_{(g)}$

At 415°C, the following initial rate data were recorded.

Experiment	$[C_2H_4O]_0$ (mol/L)	Initial rate (mol/(L • s))
1	0.002 85	5.84×10^{-7}
2	0.004 28	8.76×10^{-7}
3	0.005 70	1.17×10^{-6}

Determine the rate law equation and the rate constant at 415°C.

Checkpoint

Chlorine dioxide, ClO_2, reacts with hydroxide ions to produce a mixture of chlorate and chlorite ions.

$$2ClO_{2(aq)} + 2OH^-_{(aq)} \rightarrow ClO_3{}^-_{(aq)} + ClO_2{}^-_{(aq)} + H_2O_{(\ell)}$$

The rate data in the table below were determined at a constant temperature. Find the rate law equation and the value of *k*.

Experiment	Initial $[ClO_2]$ (mol/L)	Initial $[OH^-]$ (mol/L)	Initial rate of formation of products (mol/(L•s))
1	0.0150	0.0250	1.30×10^{-3}
2	0.0150	0.0500	2.60×10^{-3}
3	0.0450	0.0250	1.16×10^{-2}