# CHAPTER 6     RATES OF CHEMICAL REACTIONS
Expressing and Measuring Reactions Rates

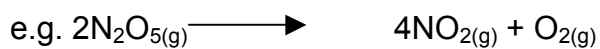Rate =

i.e.    Rate of Reaction =

=

- Use molar concentrations [   ]  to express rates

## REACTION RATES IN TERMS OF PRODUCTS AND REACTANTS

e.g. $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

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$\therefore$ production of $NO_2$ is 4 times that of $O_2$

and production of $O_2$ is $\dfrac{1}{4}$ rate of $NO_2$

- when 1 mole of $O_2$ is produced, 2 moles of $N_2O_5$ are consumed.

∴ the rate of production of $O_2$ is half the rate of disappearance of $N_2O_5$
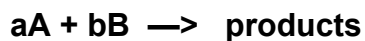
( - number due to decrease in [ ] of reactants )

e.g.

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

$NO_2$ is produced at a rate of $5.0 \times 10^{-6}$ mol/L•s. What is the corresponding rate of disappearance of $N_2O_5$ and rate of formation of $O_2$ ?

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## FACTORS THAT AFFECT RATES OF REACTION:

1)

2)

3)

4)

5)

## 6.2    THE RATE LAW: REACTION CONCENTRATION AND RATE

**aA + bB —>   products**

- 

- therefore

## RATE LAW EQUATION

- .

- .

- 

ie.    An exponent of 1 means 1$^{st}$ order w.r.t. that reactant
       An exponent of 2 means 2$^{nd}$ order w.r.t. that reactant

## RATE CONSTANT:

k      -

       -                                    -

       -                                    -

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- rate constant remains the same at a given temp.

Temp change?  – k will change because rate will change
        ∴ reactions must remain at a constant temp
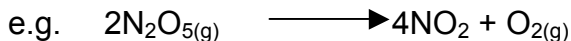- k must be given with a temp.

e.g.    $2^{nd}$ order decomposition of hydrogen iodide

k= $2.7 \times 10^{-3}$ (L/mol•s) at 440 $^{o}$C

k= $23.9 \times 10^{-3}$ (L/mol•s) at 500 $^{o}$C

## DEFINING FIRST-ORDER REACTIONS:

$1^{st}$ order    -    overall order =    1

e.g.    $2N_2O_{5(g)} \longrightarrow 4NO_2 + O_{2(g)}$

$1^{st}$ order by expt.

e.g.  $(CH_3)_3CBr_{(l)} + H_2O_{(l)} \longrightarrow (CH_3)_3OH_{(aq)} + H^+_{(aq)} + Br^-_{(aq)}$
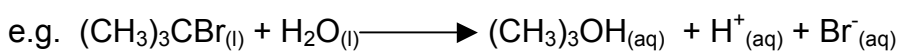
$1^{st}$ order        0 order

## DEFINING SECOND-ORDER REACTIONS

second-order reaction    -    overall order -    2

eg.    $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$
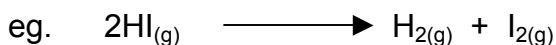
• by expt. determined $2^{nd}$ order in HI

eg.    $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$
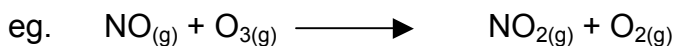
Rate determined to be second order

•

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## INITIAL RATES METHOD

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Rate expt:    $2N_2O_{5(g)}$    $\longrightarrow$    $4NO_2 + O_{2(g)}$

Rate = $k[N_2O_5]^m$  3 experiments

| Expt | Initial $[N_2O_5]$ (mol/L) | Initial rate (mol/L•s) |
|------|----------------------------|------------------------|
| 1 | 0.010 | $4.8\times10^{-6}$ |
| 2 | 0.020 | $9.6\times10^{-6}$ |
| 3 | 0.030 | $1.5\times10^{-5}$ |

• 

$\therefore 1^{st}$ order relationship (linear)

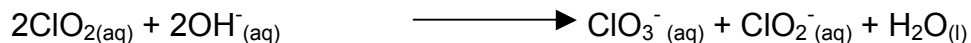• also possible to compare rate law equation for each expt. using ratios

   i.e.

**DETERMINING THE RATE CONSTANT**
   • 

   • use data from expt.'s to calculate k
Expt #1:

## eg.    finding a new law equation

$2ClO_{2(aq)} + 2OH^-_{(aq)}$ ———————→ $ClO_3^-_{(aq)} + ClO_2^-_{(aq)} + H_2O_{(l)}$
- **Expt. data at a constant temp. Find the rate law equation and value of k.**

| Expt | Initial $[ClO_2]$ (mol/L) | Initial $[OH^-]$ (mol/L) | Initial rate (mol/L•s) |
|------|------------------------|----------------------|----------------------|
| 1    | 0.0150                 | 0.0250               | $1.30 \times 10^{-3}$ |
| 2    | 0.0150                 | 0.0500               | $2.6 \times 10^{-3}$  |
| 3    | 0.0450                 | 0.0250               | $1.16 \times 10^{-2}$ |

We know:  Rate = $[ClO_2]^m[OH^-]^n$
- we want to find the values of m & n therefore we have to determine the order of the rate when one is constant and the other varies
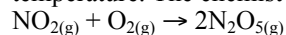
∴reaction is first order w.r.t. to $[OH^-]$

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∴

Therefore rate law equation is:

- Solve for value of k using expt. Data
- Pay close attn. to the units.

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## Rate Law Equations

**1.** A chemist carries out three trials to determine the rate of the reaction of nitrogen dioxide and oxygen at a fixed temperature. The chemist's results are shown in the chart below.
$NO_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{5(g)}$

| Experiment | Initial [NO₂] (mol/L) | Initial [O₂] (mol/L) | Initial rate of formation of N₂O₅(mol/(L ÷ s)) |
|---|---|---|---|
| 1 | 0.025 | 0.011 | $3.1 \times 10^{-4}$ |
| 2 | 0.025 | 0.022 | $6.2 \times 10^{-4}$ |
| 3 | 0.050 | 0.011 | $6.2 \times 10^{-4}$ |

**(a)** Write the rate law expression for the reaction. Explain your logic or show your calculations.

**(b)** Calculate the rate constant

**(c)** A chemist runs a trial of the reaction (at the same temperature) in which the initial concentration of $[NO_2]$ is 0.0323 mol/L and the initial concentration of $[O_2]$ is 0.0157 mol/L. Predict the initial rate.

**2.** A reaction has the following rate law:
$Rate = k[A][B]^2$

Assuming a constant temperature, by what factor does the reaction rate change when the following changes are made to initial reactant concentration?

**(a)** [A] is tripled and [B] is doubled. How does the rate change?

**(b)** [B] is halved and [A] remains the same. How does the rate change?

**(c)** [A] is quadrupled and [B] is halved. How does the rate change?

**(d)** [A] and [B] are halved. How does the rate change?

**3.** Consider the following reaction and its corresponding rate law:

$BrO_3^-{}_{(aq)} + 5Br^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3Br_{3(aq)} + 3H_2O_{(l)}$

$Rate = k[BrO_3^-][Br^-][H^+]^2$

**(a)** What is the reaction order with respect to each reactant?

**(b)** What is the overall order of the reaction?

**(c)** Suggest two different ways to track the rate of this reaction experimentally

Answers

**1. (a)** Consider experiments 1 and 3. $[O_2]$ remains the same, while $[NO_2]$ doubles. The rate also doubles. Therefore, the reaction is first order in $NO_2$.

Consider experiments 1 and 2. $[NO_2]$ remains the same, while $[O_2]$ doubles. The rate also doubles. Therefore, the reaction is first order in $O_2$.

The rate law expression is: rate $= k[O_2][NO_2]$

**(b)** 1.1 L/(mol • s)     **(c)** $5.6 \times 10^{-4}$ mol/(L • s)

**2. (a)** multiplied by a factor of 12

**(b)** multiplied by a factor of 0.25

**(c)** no change

**(d)** multiplied by a factor of 0.125

**3. (a)** first order in bromate and bromide ions, second order in hydrogen ions

**(b)** fourth order

**(c)** monitor changing pH, monitor changing conductivity

Concentration and The Rate of a Chemical Reactioin

In this experiment, you will alter the concentration of a reactant and determine its affect on the rate of the reaction, thus determining the order of the reaction and the rate law expressioin. The reaction to be examined is the reaction between the thiosulfate ion ($S_2O_3{}^{2-}{}_{(aq)}$) found in a sodium thiosulfate solution and the hydrogen ion ($H^+{}_{(aq)}$) found in a solution of hydrochloric acid. The balanced equation is given below.

$$Na_2S_2O_{3(aq)} + 2\ HCl_{(aq)} \longrightarrow H_2O_{(l)} + SO_{2(g)} + 1/8 S_{8(s)} + 2\ NaCl_{(aq)}$$

If the spectator ions are eliminated from the equation, the resulting net ionic equation is:
$$S_2O_3{}^{2-}{}_{(aq)} + 2\ H^+{}_{(aq)} \longrightarrow H_2O_{(l)} + SO_{2(g)} + 1/8\ S_{8(s)}$$
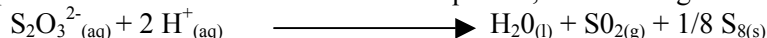
When the two colourless solutions of sodium thiosulfate and hydrochloric acid are mixed, the ensuing reaction produces solid sulphur, which causes the solution to become opaque, thus blotting out the "X" marked on a paper under the reaction flask. By measuring and recording the time that it takes for the "X" to disappear, the reaction rates can be compared for different concentrations of the thiosulfate ion.

Apparatus
50 mL beaker                                    graduated micropipettes
10 mL graduated cylinder                 thermometer
stopwatch or timer

Materials
sheet of white paper with a large dark "X" printed on it
2.00 mol/L hydrochloric acid
0.250 mol/L sodium thiosulfate

The Effect of Concentration on Reaction Rate
In this part of the experiment, the concentration of thiosulfate ion will be changed during five successive trials to see what effect thiosulfate ion concentration has on reaction rate.

**Procedure**
1. Measure out 10.0 mL of the thiosulfate solution and place it in a 50 mL beaker.
2. Add 1.0 mL of the hydrochloric acid solution to the beaker. Simultaneously, note the time.
3. Stir the solution by swirling the beaker briefly and immediately place the beaker over the "X" on the paper. Look down vertically at the "X" and note the time when the "X" is no longer visible.
4. Repeat this and every step twice and determine the average time for each concentration.
5. Repeat the above procedure using 8.0, 6.0, 4.0 and 2.0 mL of 0.250 mol/L thiosulfate solution made up to a total volume of 10.0 mL by adding distilled water.

**Calculations**
1.    For each trial, calculate the sodium thiosulfate concentration at the instant the hydrochloric acid and sodium thiosulfate have been added. The total final volume in all cases is 11.0 mL.
2.    Since we assume the concentration of sodium thiosulfate is 0.00 mol/L when the "X" disappears, the rate can be determined for each trial using the following equation.

$$Rate = \frac{concentration\ of\ sodium\ thiosulfate\ consumed\ (mol/L)}{time\ for\ the\ ``X"\ to\ disappear\ (\ s)}$$

3.    Make a table of thiosulfate ion concentration, average reaction time and reaction rate. Make sure to show the calculation for rate one time.
4.        Make a graph of initial concentration of sodium thiosulfate (x-axis) vs. reaction rate ( y-axis). Draw the line of best fit.
5.        What does this graph tell you about the reaction order with respect to the thiosulfate? Assume the rate law expression is rate $\alpha$ $[S_2O3{}^{2-}{}_{(aq)}]^m$. Determine the value of m.
6.        Determine the value of k.