

6.3 Rate Laws and Order of Reaction

- A balanced chemical equation tells us the number of moles of reactants that are used and the number of moles of products that are formed in a reaction.
- The rate of reaction for each entity can be determined but it does not tell us how the rate of the reaction may be affected if the concentration of reactants change
- Only from the analysis of experimental evidence can a reaction rate be determined

Reaction Rate Law

- From experimental evidence the rate, r , will always be proportional to the product of the **initial** concentrations of the reactants, where these concentrations are raised to some exponential values.
- This is expressed as... $\text{rate} \propto [A]^m[B]^n$
- E.g. $aA + bB \rightarrow \text{products}$

$\rightarrow \frac{\text{rate}}{[A]^m[B]^n} = \text{Constant } (k)$

$\text{rate} \propto [A]^m[B]^n$

$\text{rate} = k[A]^m[B]^n \leftarrow$
- $[A]$ and $[B]$ are the concentrations of the reactants.
- “a” and “b” are the coefficients
- m and n are the powers the concentration is raised by and is **determined experimentally**. They are also known as “order” and their sum is known as the “overall reaction order”.
- k is the rate constant
 - valid for only a specific reaction at a specific temperature.
 - * • Connects the variables of the equation
 - Unit = depends on the overall reaction order

What does it mean?

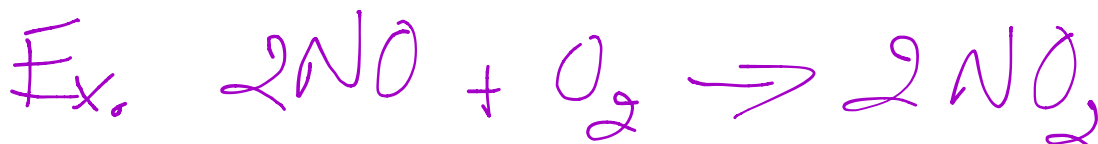


If you determine the rate law equation to be $r = k[X]^1[Y]^2[Z]^0$

- Because $r \propto [X]^1$ then if the concentration is doubled the rate will double (2^1) or if the concentration is tripled the rate will triple (3^1).
- Because $r \propto [Y]^2$ then if the concentration is doubled the rate will multiply by 4 (2^2) or if the concentration is tripled the rate will multiply by 9 (3^2).
- Because $r \propto [Z]^0$ then if the concentration is doubled the rate will multiply by 1 (2^0) or if the concentration is tripled the rate will multiply by 1 (3^0).
- Since $[Z]$ has no impact on the rate you discard it, therefore the equation should be $r = k[X]^1[Y]^2$ which has an overall reaction order of 3.
- E.g. You determine the rate law equation to be $r = k[A]^1[B]^2$, if you triple the concentration of B what will happen to the rate?
 $r \propto [B]^2$ then $3^2=9$ so the reaction rate will multiply by 9 (9 times faster)
- Order is not an absolute fundamental property. It is a convenient way to describe the rate reaction.
 - first order reactions $r = k[x]^1$
 - second order reactions $r = k[x]^2$ or $r = k[x]^1[y]^1$
 - third order reactions $r = [x]^3$ or $r = k[x]^2[y]^1$

Experimental Determination of Reaction Order

- The overall order of a reaction can be determined only from experimental data.
- E.g. The formation of NO in car engines is the first step in the formation of smog. NO is easily oxidized to nitrogen dioxide by the reaction $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$. The following data were collected in a study of reaction rates.



- a) What is the rate law for the reaction?
b) What is the rate constant?

Initial Concentrations (mol/L)		Rate of Formation of NO_2 ($\text{mol L}^{-1} \text{s}^{-1}$)
$[\text{O}_2]$	$[\text{NO}]$	
0.0010	0.0010	7.10
0.0040	0.0010	28.4
0.0040	0.0030	255.6

Solution

Initial Concentrations (mol/L)		Rate of Formation of NO_2 ($\text{mol L}^{-1} \text{s}^{-1}$)
$[\text{O}_2]$	$[\text{NO}]$	
0.0010	0.0010	7.10
0.0040	0.0010	28.4
0.0040	0.0030	255.6

a) rate law: $r = k [\text{O}_2]^m [\text{NO}]^n$
 $r = k [\text{O}_2]^1 [\text{NO}]^2$ (overall order 3)

b) rate constant: $r = k [\text{O}_2]^1 [\text{NO}]^2$
 $7.10 = k [0.0010]^1 [0.0010]^2$
 $k = \frac{7.10 \text{ mol L}^{-1} \text{s}^{-1}}{[0.0010 \text{ mol L}^{-1}]^1 [0.0010 \text{ mol L}^{-1}]^2}$
 $k = 7.1 \times 10^9 \text{ L}^2 \text{mol}^{-1} \text{s}^{-1}$

Sample Questions:

1. At a certain temperature the following data were collected for the reaction $2\text{ICI} + \text{H}_2 \rightarrow \text{I}_2 + 2\text{HCl}$.

Initial Concentrations (mol/L)		Rate of Formation of I_2 ($\text{mol L}^{-1} \text{s}^{-1}$)
[ICI]	[H ₂]	
0.10	0.10	0.0015
0.20	0.10	0.0030
0.10	0.05	0.00075

Determine the rate law and the rate constant for the reaction.

2. The reaction of iodide ion with hypochlorite ion (found in liquid bleach) follows the equation $\text{OCl}^- + \text{I}^- \rightarrow \text{OI}^- + \text{Cl}^-$.

Initial Concentrations (mol/L)		Rate of Formation of Cl^- ($\text{mol L}^{-1} \text{s}^{-1}$)
[OCl ⁻]	[I ⁻]	
1.7×10^{-3}	1.7×10^{-3}	1.75×10^4
3.4×10^{-3}	1.7×10^{-3}	3.50×10^4
1.7×10^{-3}	3.4×10^{-3}	3.50×10^4

Determine the rate law and the rate constant for the reaction.

Relating Reaction Rate to Time

- Refer to page 378
- For classroom activities – the length of time a reaction takes is easy to observe
- Rate is proportional to $1/\Delta t$
- Graph relates initial concentration and the rate with respect to the order of the reaction.
- Note - the line is not showing the change in concentration
- Looking for a straight line when plotting a set of data will determine the order of reaction

Chemical Kinetics and Half-life

- Nuclear decay and many other chemical systems have a first order process
- The rate is directly proportional to the concentration of the chemical
- The half-life is the time required for half of the sample to react and is used to describe more than just nuclear decay.
- Use the equation: $k t_{1/2} = 0.693$, where k is the rate constant and $t_{1/2}$ is the half-life of the radioisotope.
- E.g. Given the rate constant \rightarrow determine the half life \rightarrow determine amount of chemical left after a period of time
- If the mass of an antibiotic in a patient is 2.464 g, what mass of antibiotic will remain after 6.0 h, if the half life is 2.0 h, and no further drug is taken?

Number of half lives in 6.0 h = $6.0 \text{ h} / 2.0 \text{ h} = 3 \text{ half lives}$

mass = $2.464 \text{ g} \times (1/2)^3 = 0.31 \text{ g}$

There would be 0.31g remaining after 6.0 h.

Homework

- Practice 1,2,3,4,5,6,7,8
- Questions 1,2,3,4