

Revised August 2011



HONORS TOPIC 13: Kinetics

Chemical reactions can occur at significantly different rates. The basis for the study of the rate of chemical reactions (Kinetics) is collision theory.

- **Collision theory**

Collision theory suggests that a reaction will only take place if three conditions are met;

1. The reactants come into contact (they collide).
2. The collision occurs with a certain minimum energy, known as the activation energy, E_{act} .
3. The collision has the correct collision geometry. This means that the reactants must collide in a certain physical orientation for a reaction to take place.

If reactants do not collide, or collide with energies lower than the activation energy or collide without the correct collision geometry, then no reaction will occur. These collisions are described as unsuccessful, that is, they do not lead to a chemical reaction.

- **Factors controlling rate of reaction**

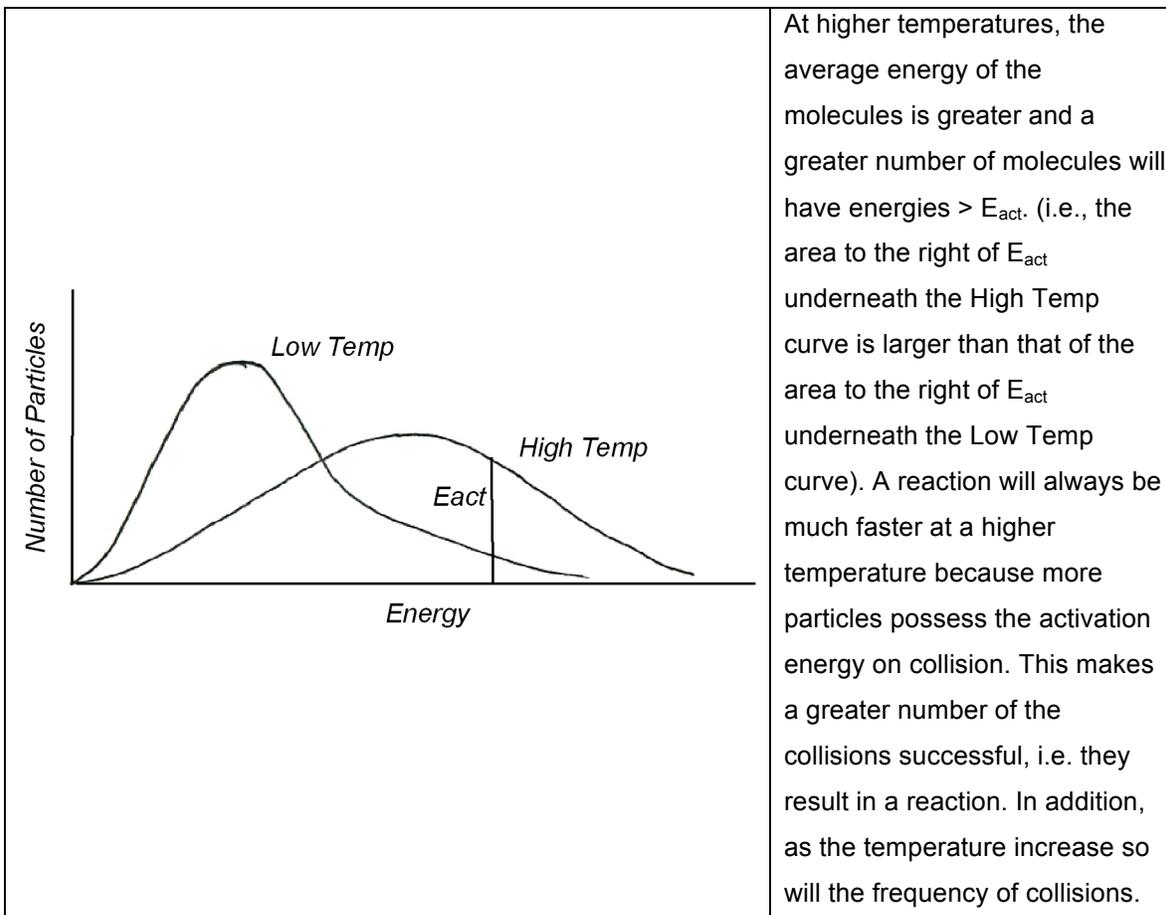
1. Concentration

Increasing the reactants concentration by putting more reactants into the same space increases the collision frequency, leading to a faster rate of reaction. A similar effect is observed when increasing the pressure in a gaseous reaction. Increasing the pressure of a gas can be achieved by reducing its volume whilst leaving the number of particles the same.



2. Temperature

A rise in temperature will result in an increased rate of reaction. As a guideline in many reactions a 10°C rise will result in an approximate doubling of the rate. Consider the Maxwell-Boltzmann distribution plot of energies. The area underneath the curve represents the total number of molecules.

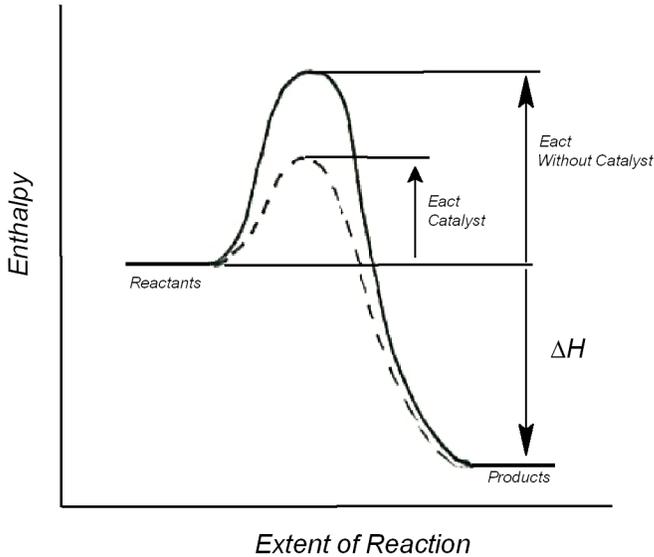
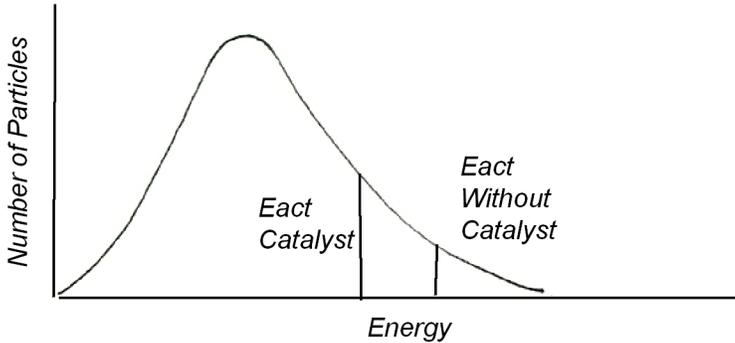


3. Solid particle size

When a solid reacts, only the particles on the surface of the solid are available for reaction. If the solid is broken up into smaller pieces its surface area gets larger and more particles are available for collision, therefore the reaction rate increases.



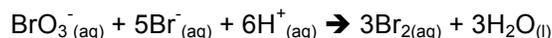
4. Catalysis

 <p>The graph plots Enthalpy on the y-axis and Extent of Reaction on the x-axis. A horizontal line represents the energy level of Reactants, and a lower horizontal line represents the energy level of Products. The vertical distance between these two lines is labeled ΔH. Two curves start at the Reactants level and end at the Products level. The solid curve represents the reaction without a catalyst, with its peak labeled E_{act} Without Catalyst. The dashed curve represents the reaction with a catalyst, with its peak labeled E_{act} Catalyst. An arrow points from the catalyst peak to the uncatalyzed peak, indicating the lower activation energy.</p>	<p>Catalysts are substances that increase the rate of a reaction whilst remaining chemically unchanged. Catalysts usually work by providing an alternative reaction route that requires a lower activation energy. Therefore a greater number of molecules will possess the lower E_{act} and a greater number of collisions will result in reaction (i.e. be successful).</p> <p>Note that ΔH for the same uncatalyzed or catalyzed reaction is the same.</p>
 <p>The graph plots Number of Particles on the y-axis and Energy on the x-axis. A single bell-shaped curve represents the distribution of particle energies. Two vertical lines are drawn from the x-axis to the curve. The line on the left is labeled E_{act} Catalyst, and the line on the right is labeled E_{act} Without Catalyst. The area under the curve to the right of the catalyst line is shaded, representing the number of particles with sufficient energy to undergo the reaction.</p>	<p>Providing a pathway of lower activation energy means that a greater number of particles will now possess the required minimum energy and the reaction will have a greater reaction rate.</p>



- **The rate equation and orders of reaction**

A very common reaction for investigating rates is the reaction below between bromate ions and bromide ions in acid solution.



The results of some kinetics experiments are given in the table below.

Mixture	Initial concentrations			Rate in M per unit time
	[BrO ₃ ⁻] / M	[Br ⁻] / M	[H ⁺] / M	
A	0.0050	0.025	0.030	10
B	0.010	0.025	0.030	20
C	0.010	0.050	0.030	40
D	0.010	0.050	0.060	160

Inspection treatment of initial rate data

By comparing the results from mixtures A & B;

Doubling [BrO₃⁻] doubles the rate. (Note the other concentrations are kept constant to ensure a fair test). Therefore the rate \propto [BrO₃⁻] and the rate is said to be first order with respect to, (w.r.t), [BrO₃⁻].

By comparing the results from mixtures B & C;

Doubling the [Br⁻] doubles the rate. (Note the other concentrations are kept constant to ensure a fair test). Therefore the rate \propto [Br⁻] and the rate is said to be first order w.r.t [Br⁻].

By comparing the results from mixtures C & D;

Doubling the [H⁺] quadruples the rate. (Note the other concentrations are kept constant to ensure a fair test). Therefore the rate \propto [H⁺]² and the rate is said to be second order w.r.t [H⁺].

Combining these results gives, Rate \propto [BrO₃⁻][Br⁻][H⁺]² and introducing the rate constant (k), the equation becomes, Rate = k[BrO₃⁻][Br⁻][H⁺]²

This is known as the rate equation (or rate law) and all rate equations take the general form;



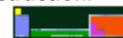
$$\text{Rate} = k[\text{A}]^x[\text{B}]^y[\text{C}]^z$$

Where k is the rate constant and x , y and z are the orders with respect to the reactants A, B and C. The order with respect to a given reactant is the power to which the concentration of that reactant is raised to in the rate equation. The overall order of the reaction is the sum of the individual orders.

Note:

1. It is not possible to deduce anything about the order of a reaction from the balanced chemical equation. Sometimes they will be the same but this is a coincidence. Orders must be found experimentally.
2. Units of the rate constant are important. They vary a great deal and are often the subject of many AP questions.
3. A reactant that has no effect on the rate is said to have an order equal to zero. It has no effect on the rate and since any number raised to the power of 0 is equal to 1 it can be omitted from the rate equation.
4. Orders can be fractional (e.g. $\frac{1}{2}$) – **see 2009, 3(e)(ii).**

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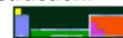
Task 13a

1. For the reaction between X and Y data has been collected in the table below. Deduce the orders of reaction with respect to each reactant, the overall order, the rate equation, a value for the rate constant and the units of the rate constant.

Experiment	Starting [X] / M	Starting [Y] / M	Rate / M min⁻¹
1	0.00500	0.0250	1.00
2	0.0100	0.0250	4.00
3	0.00500	0.0125	1.00

2. For the reaction between A and B data has been collected in the table below. Deduce the orders of reaction with respect to each reactant, the overall order, the rate equation, a value for the rate constant and the units of the rate constant.

Experiment	Starting [A] / M	Starting [B] / M	Rate / M s⁻¹
1	0.00500	0.0250	1.00
2	0.01000	0.0250	2.00
3	0.00500	0.0125	0.500



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Mathematical treatment of initial rate data

Rather than doing an inspection followed by a verbal interpretation of initial rate data, it is also possible to treat the data mathematically in order to find the orders with respect to each reactant by finding the ratio of the rate equations. For example in question #1 in Task 13a;

By comparing experiments 2 and 1, we find;

$$\frac{\text{Rate}_{\text{Expt. 2}} = 4.00 = k [0.0100]^a [0.0250]^b}{\text{Rate}_{\text{Expt. 1}} = 1.00 = k [0.00500]^a [0.0250]^b}$$

Where a and b are the orders with respect to [X] and [Y] respectively, and k is the rate constant.

This allows the simplification of the expression to read;

$$\frac{\text{Rate}_{\text{Expt. 2}} = 4.00 = k [0.0100]^a \cancel{[0.0250]^b}}{\text{Rate}_{\text{Expt. 1}} = 1.00 = k [0.00500]^a \cancel{[0.0250]^b}} = 4 = 2^a$$

Therefore a = 2, i.e. the order with respect to [X] is 2.

Repeat the process to investigate the order with respect to [Y] by comparing experiments 1 and 3;

$$\frac{\text{Rate}_{\text{Expt. 1}} = 1.00 = k [0.00500]^a [0.0250]^b}{\text{Rate}_{\text{Expt. 3}} = 1.00 = k [0.00500]^a [0.0125]^b}$$

Where a and b are the orders with respect to [X] and [Y] respectively, and k is the rate constant.

This allows the simplification of the expression to read;

$$\frac{\text{Rate}_{\text{Expt. 1}} = 1.00 = k \cancel{[0.00500]^a} [0.0250]^b}{\text{Rate}_{\text{Expt. 3}} = 1.00 = k \cancel{[0.00500]^a} [0.0125]^b} = 1 = 2^b$$

Therefore b = 0, i.e. the order with respect to [Y] is 0.

Task 13b

Using a mathematical treatment of the data in question #2 of Task 15a, determine the orders of reaction with respect to [A] and [B].



- **Rate equations and reaction mechanisms**

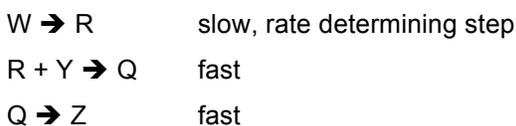
Chemical reactions proceed via a sequence of distinct stages. The sequence is known as the mechanism and each part of the mechanism is known as a "step". The rate of the reaction is only dependant upon the slowest step, also known as the *rate determining step* or RDS. As a result, only reactants that appear in the rate determining step appear in the rate equation and vice-versa.

Example #1

The reaction below



Has the following mechanism



Here the rate only depends on the concentration of W (since it is the only reactant in the RDS) and therefore the rate equation only contains W.

The rate equation is, Rate = $k[W]$. The order w.r.t W is 1, since the stoichiometric coefficient of W in the rate determining step is 1.

Note: R and Q are not reactants or products, but are rather they are intermediates that are formed in one step during the reaction, but then are used up in a subsequent step.

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Example #2

The reaction below



Has the following mechanism



Here the slow step contains Q and B, and Q is an intermediate. Since Q is an intermediate it cannot feature in the rate equation (since only reactants are allowed in rate equations) so it must be replaced. Since the formation of Q is dependent on A, Q can be replaced by A in the rate equation. Therefore the rate equation is given as, $\text{Rate} = k [A] [B]$. The orders w.r.t A and B are both 1 since the stoichiometric coefficient of B in the rate determining step is 1, and the stoichiometric coefficient of A (which Q depends upon) is also 1.

Note:

1. In all valid mechanisms the sum of the individual fast and slow steps must be the same as the overall chemical equation.
2. The stoichiometric number of a substance that appears in the slow step is the power that the concentration of that substance is raised to in the rate equation.
3. If a substance is present at the beginning of a reaction AND present in the same form at the end of the reaction, it can be identified as a catalyst.



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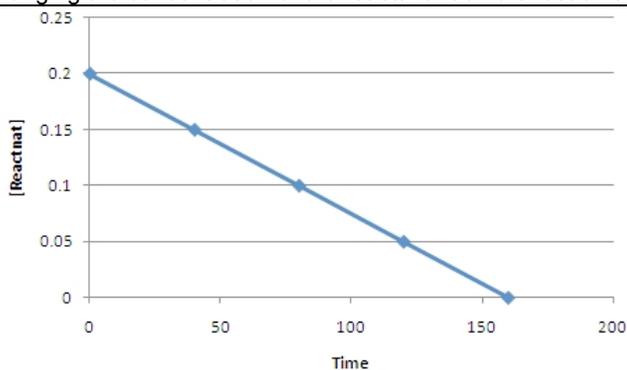
- Graphs and kinetic data

1. Plotting the concentration of a reactant ([Reactant]) against time.

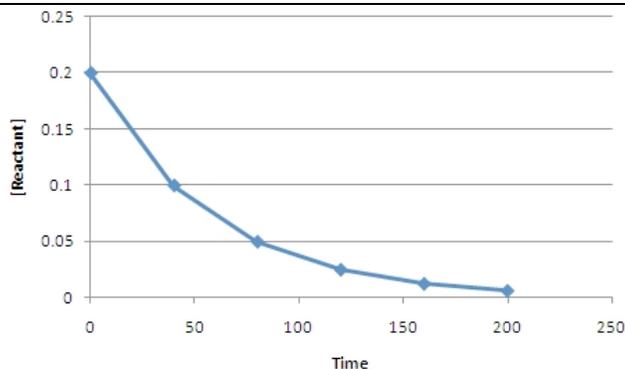
One way of defining the rate is to use the expression below and therefore the gradient (slope) of such a graph will equal the rate.

$$\text{Rate} = \frac{\text{decrease in concentration of reactant}}{\text{time}}$$

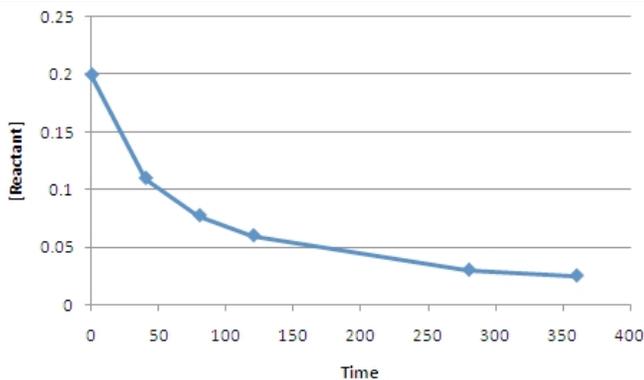
ZERO ORDER. A straight-line shows zero order w.r.t that reactant. The slope of the graph is constant, i.e. the rate is constant so changing the concentration of the reactant has no effect on the rate.



FIRST ORDER. A constant half-life graph shows first order w.r.t that reactant. The graph shows constant a constant half-life.



SECOND ORDER. A graph that looks very similar to the first order graph, BUT on closer inspection one finds that the half-life is NOT constant.



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2. Plotting initial rates against concentrations of the reactants.

