

Reaction Kinetics

Rate

Rate indicates the rapidity of a reaction taking place. The rate can be in terms of a rate of change of:

- moles or mass of a reactant or product
- concentration of a reactant or product
- pressure
- colour
- density
- electrical conductivity
- pH

$$\text{Rate} = \frac{\Delta \text{ something}}{\Delta \text{ time}}$$

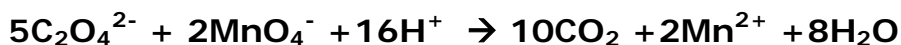
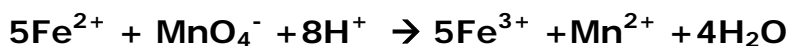
Factors affecting Rates

A. Nature of reactant

Some reactions are very fast while others are surprisingly slow. This is often due to the types of reactants involved.

Ex. Rate of Li and water reaction vs. K and water
Melting of ice to water vs diamond to graphite
As a general rule, ion precipitation reactions tend to be faster than reactions between solids or gases.

*** If a reactant has many bonds that need to be broken compared to another reactant with fewer bonds, then the reactant that involves fewer bond breakages will be faster and have the higher rate.



Both reactions involve MnO_4^- ion. However, the first reaction involves only electron transfer (RedOx), while the second reaction involves bond breakages.

Nature of reactants \leftrightarrow rate of reaction

B. Concentration of Reactant(s)

Alka seltzer is an antacid, it reacts to neutralize acid and produces a gas. The rate of this reaction can be monitored by seeing how long it takes for the tablet to react completely. This is done using 6M and 0.1M HCl

Increase in Concentration → Increase in reaction rate

C. Temperature of Reactant

At low temperatures the rate is low, the reaction is slow(er). Increasing the temperature ALWAYS increases the Rate of reaction.

Increase in temperature → Increase in reaction rate

D. Presence of a Catalyst

A catalyst increases the rate without itself being consumed. This requires that the catalyst be re-generated further on in the reaction if it is initially altered or consumed.

Ex. hydrogen peroxide, H_2O_2 spontaneously decomposes at room temperature to produce water and oxygen gas. When it is placed on a cut, the catalyst (catalase) in the blood causes the reaction to happen more rapidly. Manganese (IV) oxide, MnO_2 will also act as a catalyst for this reaction.

Presence of a catalyst → Increase in reaction rate

E. Surface Area of Reactant(s)

For any heterogeneous reaction (usually solid-liquid – having more than one phase, or two or more separate materials in the same phase) the surface area affects the rate. If the surface area is increased by powdering, grinding etc... then the rate increases

Ex. Combustion of lycopodium powder

Increase in Surface Area → Increase in reaction rate

Collision Theory and Temperature

The kinetic energies of molecules within a gaseous sample are distributed as follows:

Only those particles whose E_k (kinetic energy) exceeds E_a (activation energy) will have enough kinetic energy to react. The molecules to the LEFT of the threshold (E_a) may collide, but these collisions will not lead to product.

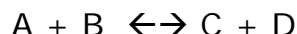
1. *At low temperatures (T_1):* few molecules have sufficient energy to collide effectively and react; few molecules exceed the threshold energy.
2. *At high temperatures (T_2):* the entire molecular distribution shifts to the right. More molecules exceed the threshold, the collision frequency is increased causing a higher rate of reaction.

However, of those particles that do exceed the threshold, some still don't react on collision. This is due to their improper collision geometry

Then, only those particles that both exceed the threshold AND have favorable collision geometry will collide effectively and produce products.

Potential Energy in Reactions

Consider the exothermic reaction between two fictitious molecules A and B



1. As the A and B molecules approach each other during the collision process, their potential energy increases. This is due to the increase in repulsive force between their electron clouds as the molecules come nearer to each other. The increase in E_p (potential energy) results in a decrease of their kinetic energy, they slow down. If the molecules have sufficient initial E_k and a favorable geometry, they will be able to form a short lived intermediary species called the *activated complex* on collision.

Once the activated complex is formed, the cluster will break apart (new bonds form) and the particles separate, simultaneously lowering their E_p and increasing their E_k and speed. Since the products have less E_p than the reactants had, some energy is released during this reaction. The difference in products and reactants E_p is called *enthalpy* = ΔH

2. As the forward reaction proceeds, products form. When the products (C + D) collide, they react in a reverse reaction to produce A + B. Eventually a situation will develop where both forward and reverse rates are equal and no further noticeable changes occur. We call this Equilibrium, more on that later

3. The activation energy is the energy required to reach the activated complex. For this example, the forward E_a is 60kJ and for the reverse reaction the E_a is 80kJ. The lower forward activation energy allows MORE molecules to react in the forward direction than will react in the reverse. The forward reaction is favoured.
4. The ΔH for a reaction is the difference in energy content between that of the products and that of the reactants.

$$\Delta H = H_{\text{PRODUCTS}} - H_{\text{REACTANTS}}$$

For this exothermic case the products have 20kJ of energy and the reactants have 40kJ.

Then, the $\Delta H = 20\text{kJ} - 40\text{kJ} = -20\text{kJ}$

The ΔH is negative for an exothermic reaction and positive for an endothermic reaction

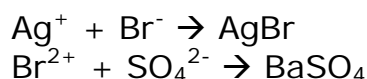
Ex.



Reaction Mechanism

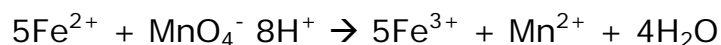
A reaction mechanism is the sequence of steps by which a multi-step reaction proceeds. Few reactions proceed in only one step. Generally, reactions involve a sequence of steps. Those few reactions that do proceed in only one step do so because only 2 particles are involved in the collision. Any 2 particle reaction is an *elementary process*. Reactions involving many steps must then involve numerous elementary processes, one following the other.

Elementary Process (*involving only 2 particles*)



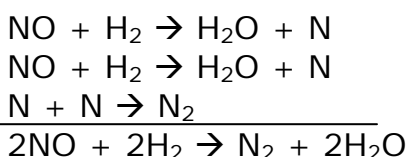
These two reactions involve only 2 particles. They are elementary processes. Each represents the true reaction; they represent the mechanism by which the reaction proceeds.

Not an Elementary Process (*example has 14 particles*)

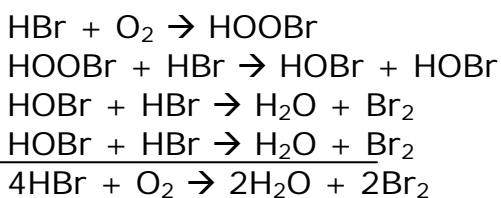


This reaction involves a 14 particle collision. This is highly unlikely, imagine 14 cars colliding simultaneously at an intersection. What is more likely is that 2 particles collide to form an *intermediary*. The intermediary then collides with another particle until the sum of all the elementary process yields the entire reaction. The slowest step in such a sequence is the *rate determining step*.

Ex. $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ (the intermediary is N)
A possible mechanism is:

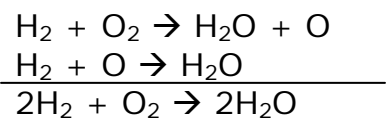


Ex. $4\text{HBr} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2$ (intermediaries are HOBr and HOBr)
A possible mechanism is:



Ex. $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ (intermediary is O)

A possible mechanism is:



Notice that in all examples the intermediary is first **produced** then **used up** in a subsequent step.

Catalysts

A *catalyst* is a substance that speeds up a reaction without being consumed, it's effectively the opposite of an intermediary. This is accomplished by introducing an *alternate reaction mechanism* which has a lower activation energy. Because the activation energy is less for a catalyzed reaction, more particles will now form the activated complex and proceed to form products. The ΔH for a catalyzed reaction will not be changed from its uncatalyzed value, as the potential energies for reactants and products do not change.

Although a catalyst is present, the uncatalyzed path is still present. What happens is that most molecules will simply follow the catalyzed path hence the higher rate.

Removing the catalyst removes the alternate path with the lower activation energy, and the rate will decrease again.

When a reaction is catalyzed, the forward reaction rate will increase, but so will the reverse rate. Chemists do not use catalysts to produce more of a product, but to increase its rate of formation.