I. Introduction to Reaction Rate

What is reaction rate?

- Rate is related to how long it takes for a reaction to go to completion.
- Measured in terms of:
  - rate of consumption of reactants per second
  - rate of production of products per second
- Units can be anything that can be measured per unit of time. Common examples are:
  - g/s, mL/s, kPa/s, and so on...
  - sometimes if the reactant monitored is difficult to measure and we want a relative rate with respect to the reactant the unit s^{-1} is used.

Monitoring Reactions

Different reactions will require different methods of determining the reaction rate. This requires you to have a general working knowledge of different types of reactions, and various chemical species.

For example:

- knowing that Cu^{2+} is a blue coloured ion, Cu metal is reddish brown, and CuO is black
- knowing that acid + base → salt + water , and understanding that H^+ and OH^- concentration will decrease as the reaction proceeds because they react to form water.

The following are some of the more common methods of observing the rate of a reaction:

1) Colour Change

- a spectrophotometer is used to measure the INTENSITY of the colour in a solution. A spectrophotometer works by shining light through a small sample of liquid. The more colour intensity the more the light is absorbed. This means that as the coloured species in a reaction is formed or used up in a reaction the intensity of colour will change.
- Increasing colour intensity = lower absorption = increase in concentration of coloured species.
- Example of a reaction where there is a colour change:

$$\underset{\text{colourless}}{AgNO_{3(aq)}} + Cu_{(s)} \rightarrow Ag_{(s)} + \underset{\text{blue/green}}{Cu(NO_3)_{2(aq)}}$$

Rate is calculated using:

$$\text{Rate} = \frac{\Delta\,\text{colour change}}{\Delta\,\text{time}}$$

2) Temperature Change

- for exothermic reactions the temperature will increase
- for endothermic reactions the temperature will decrease

An example of a reaction that has a temperature change is:

$$CH_{4(g)} + 3O_{2(g)} \rightarrow CO_{2(g)} + 4H_2O_{(l)} + \text{heat}$$

Rate is measured using:

$$\text{Rate} = \frac{\Delta\,\text{temperature}}{\Delta\,\text{time}}$$

3) Pressure Change

- gas produced means the pressure increases
- gas consumed means the pressure decreases

An example of a reaction that has a pressure change is:

$$\underbrace{Mg_{(s)} + 2HCl_{(aq)}}_{\text{no gas on reactant side}} \rightarrow MgCl_{2(aq)} + \underbrace{H_{2(g)}}_{\text{gas produced}}$$

Rate is measured using:

$$\text{Rate} = \frac{\Delta\,\text{pressure}}{\Delta\,\text{time}}$$

4) Mass Change

- mass increases if the oxygen in the air reacts with a material
- mass decrease if a gas produced escapes from the container

Examples of reactions that have a mass change are:

$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$ (gas escapes causing mass loss)

$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$ (oxygen from the air attaches to Mg and mass increases)

Rate is measured using:

$$\text{Rate} = \frac{\Delta\,\text{mass}}{\Delta\,\text{time}}$$

II. Factors affecting Rates of Reaction

- Rate of reaction can be increased or decreased
- Several factors affect the rate of reaction:
    - temperature
    - concentration
    - pressure
    - particle size / surface area
    - nature of reactants
    - homogeneous vs heterogeneous

Home lab:

1) baking soda in cold vs hot vinegar (**never** heat vinegar in a microwave oven!)
2) regular vinegar + baking soda vs diluted vinegar and baking soda
3) piece of chalk + vinegar vs crushed chalk + vinegar

What you should know:

1) Temperature

- As the temperature increases the faster the reaction occurs, therefore the rate increases as the temperature increases
- As the temperature decreases the slower the reaction occurs, therefore the rate decreases as the temperature decreases

2) Concentration

- As the concentration decreases the reaction gets slower, therefore the rate decreases as the concentration decreases
- As the concentration increases the reaction gets faster, therefore the rate increases as the concentration increases

3) Pressure

- Pressure is like the concentration of a gas. The higher the pressure the faster the reaction, therefore as pressure increases the rate increases.
- The lower the pressure the slower the reaction, therefore as pressure decreases the rate decreases.

4) Particle Size and Surface area

- Particle size and surface area are related to each other. If I crush a piece of chalk into small pieces the amount of exposed surface area increases because the chalk that was originally trapped on the inside of the piece of chalk is now on the surface.
- As surface area increases the rate of the reaction increases

5) Nature of reactants

- Reactions occur because bonds break and reform. The rate of the reaction is related to how easy it is for the old bonds to be broken and the new bonds to form
- Phase at room temperature
- Electronegativity
- Contact between reactants – including surface area and homogeneous vs heterogeneous issues described elsewhere in this section

6) Homogeneous vs Heterogeneous

- Homogeneous reactions have particles that freely mix on a molecular level. There is no interface at which the reaction occurs. Homogeneous reactions tend to occur faster than heterogeneous reactions because there is no surface area effect. Examples of homogeneous reactions include reacting: miscible liquid with miscible liquid, gas with gas, aqueous with aqueous.
- Heterogeneous reactions occur at a surface, and the particles interact at an interface rather than freely mixing. Examples of heterogeneous reactions include reacting: solid with solid, immiscible liquids, gas with liquid, gas with solid, or any other situation where the phases of the reactants are different.

7) Catalysts

- Increase the rate of a reaction without being consumed in the reaction

8) Inhibitors

- Decrease the rate of a reaction usually by sticking to the active sites of the reactant so that it cannot react which decreases the concentration of the reactants

Reaction Rate and Phase

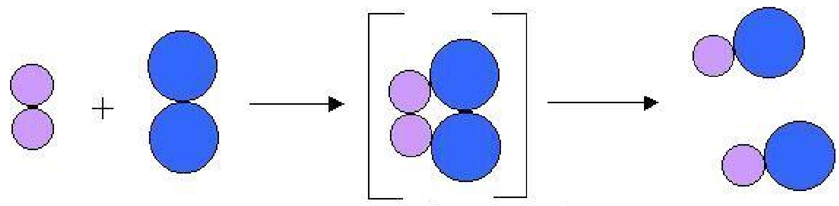
Generally,

FAST ⟶ SLOW

Aqueous >> Gases >> Liquids >> Solids

III. Collision Theory

- Particles need to collide for a reaction to occur
- Not all collisions are successful
- when a collision occurs an **activated complex** is formed which is a highly unstable complex where old bonds break and new bonds form. The activated complex falls apart to give the products.

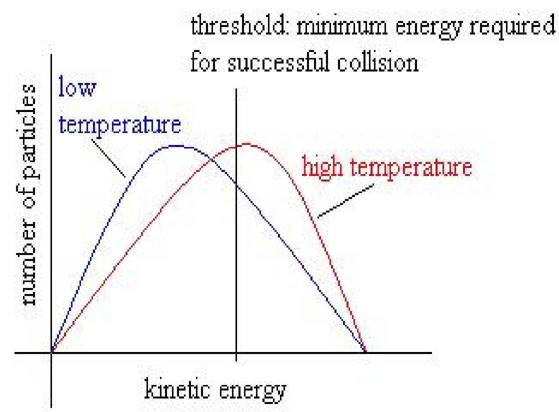


Factors Affecting the Success of a Collision

1) Temperature

- Particles need enough energy to overcome the repulsion of the electron clouds surrounding the particles
- As temperature increases the number of particles with enough energy to get over the threshold barrier increases. This means more particles are able to collide successfully and so the rate increases. See diagram on right.
- As temperature increases the number of particles that can collide successfully increases so the rate of reaction increases

Kinetic Energy Distribution Curves



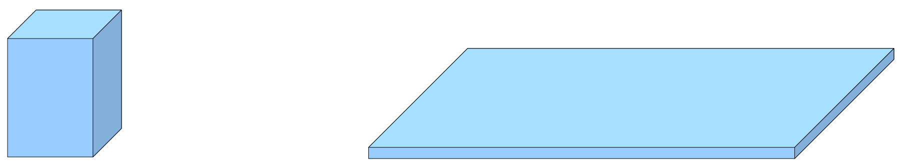
2) Concentration

Analogy: Imagine a game where you run through a shopping mall, and that you get points for bumping into people. Would you get more points running at 2pm on a Saturday afternoon or running at 9am on a Monday morning? Why? Hopefully you realize the Saturday afternoon will give you more points because there are more people filling the mall, and so you are more likely to bump into someone.

- increasing concentration means there are more particles which makes the number of collisions increase and therefore the probability of a successful collision increases

3) Surface Area

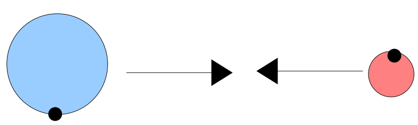
- As surface area increases the contact between reactants increases which means more collisions.
- As surface area increases rate increases because there are more collisions so the probability of a successful collision increases.
- Surface area can be increased for a solid by decreasing the size of the particles in a solid (crushing, grinding, shredding,etc.)
- Surface area can be increased for a liquid by using wider shallower container rather than a narrower deeper container.



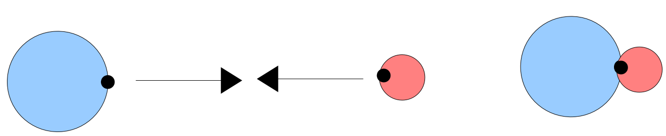
Low surface area *High surface area*

4) Geometry

- Active sites on particles have to be correctly oriented in order for a collision to cause a reaction.



No reaction even if sufficient energy because the active sites are not aligned



Reaction occurs if there is sufficient energy to overcome repulsion

IV. PE, KE, and Reaction Rate

Kinetic Energy is movement energy.

Potential Energy is stored energy.

Kinetic energy increases as potential energy decreases. Kinetic energy decreases as potential energy increases. Think about an elastic band that is stretched, when the elastic is released the energy stored causes the elastic to fly across a room.

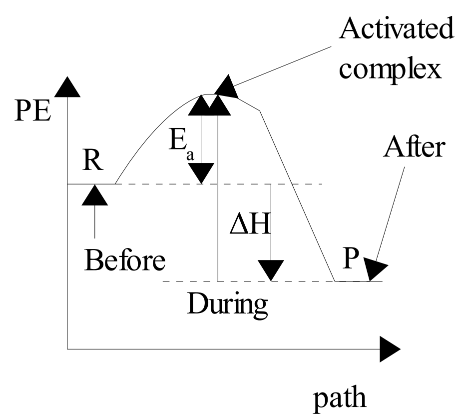
Kinetic energy and potential energy are related to each other in a collision between particles. We will look at what is going on before, during, and immediately after a collision.

Before Collision

- As the particles approach each other they repel each other because of their electron clouds. This is a force opposing motion which causes the particles to slow down and the kinetic energy decreases.
- Since energy cannot be lost the potential energy increases

During Collision

- If there is enough energy to overcome the repulsion a collision occurs
- If the geometry is good the collision is successful
- As soon as the particles collide the activated complex is formed. The activated complex has very high potential energy, and is unstable. In the activated complex old bonds break and new bonds form.



After Collision

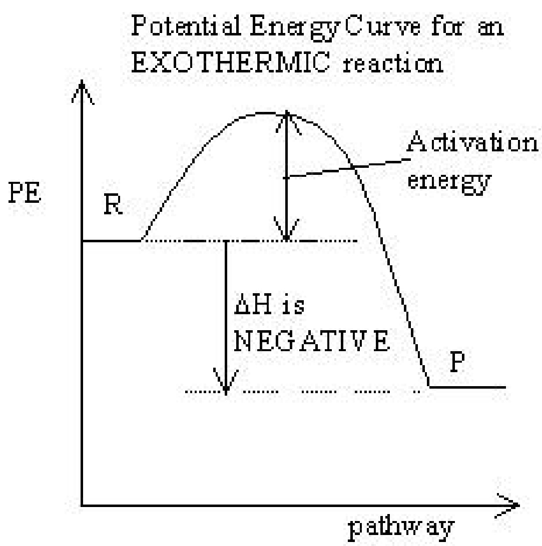
- Activated complex breaks apart and products are formed
- Potential energy decreases and kinetic energy increases because the electron clouds of the product molecules repel each other forcing the product molecules to push away from each other

Summary of Key Ideas

- reactants and products have potential energy
- energy to overcome the threshold and make the activated complex is called the activation energy E_a
- $\Delta H = H_{products} - H_{reactants}$

Enthalpy (ΔH) and Reactions

Exothermic reactions give OUT heat or other energy. The heat can be included as part of the chemical equation or listed after the equation as a ΔH value. Exothermic reactions are spontaneous and will continue to react after the reaction is started because they produce enough energy to sustain the reaction until the reactants are used up.



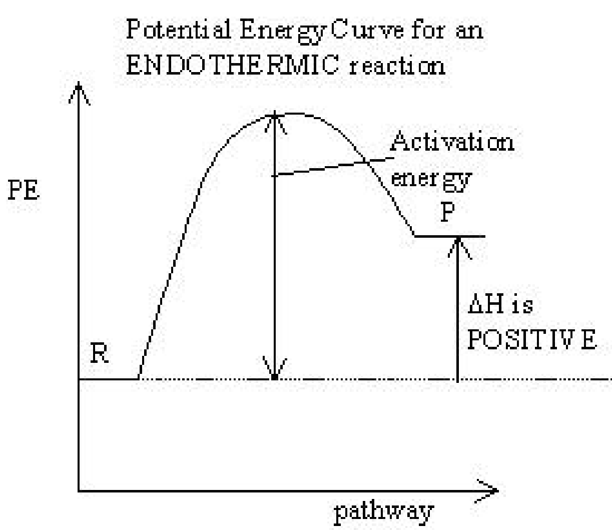
Examples of how heat is expressed in a chemical equation for and exothermic reaction are shown below:

$A + B \rightarrow AB + 100kJ$

OR

$A + B \rightarrow AB \quad \Delta H = -100kJ$

Endothermic reactions take IN heat or other energy. The heat can be included as part of the chemical equation or listed after the equation as a ΔH value. Endothermic reactions are not spontaneous and require energy to be constantly supplied in order for the reaction to continue.



Examples of how heat is expressed in a chemical equation for an endothermic reaction are shown below:

$C + D + 90kJ \rightarrow CD$

OR

$C + D \rightarrow CD \quad \Delta H = +90kJ$

V. Reaction Mechanism

- most of the time reactions involve one or a series of 2 particle collisions. These 2 particle collisions are called elementary processes.
- Multiple particle collisions are less likely to occur as a single step because the probability of three particles colliding is very low, and the probability of the three particles colliding with the correct geometry is even lower.

Elementary Processes in single step reactions:

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

$$Mg^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)} \rightarrow MgCO_{3(s)}$$

Most reactions are not this simple, and require more than one elementary process to complete the reaction. This series of elementary processes that occur to cause a reaction are called the reaction mechanism. Reaction mechanisms are usually determined experimentally.

Examples of reactions that are not a single elementary process:

1) $5Fe^{2+} + MnO_4{}^{-} + 8H^{+} \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

- There are 14 particles on the reactants side of this equation
- Reaction will probably occur as a series of elementary processes

2) $A + B + C \rightarrow ABC$

- There are 3 particles on the reactants side of this equation
- Possible mechanism could be:

Reaction intermediate
(starts RIght)

Step 1: $A + B \rightarrow AB$
Step 2: $AB + C \rightarrow ABC$

Overall: $A + B + C \rightarrow ABC$

Reaction intermediate is
used up in the reaction

Note:
- not all steps occur at the same rate
- the slowest step is known as the **rate determining step** because the overall reaction cannot be faster than the slowest step.

Examples of Mechanisms

1) Decomposition of hydrogen peroxide

Overall: $H_2O_2 \rightarrow 2H_2O + O_2$

Reaction intermediate

$$\begin{array}{ll} \text{Step 1:} & H_2O_2 \rightarrow H_2O + \cancel{O} \\ \text{Step 2:} & \cancel{O} + H_2O_2 \rightarrow H_2O + O_2 \\ \hline \text{Overall:} & H_2O_2 \rightarrow 2H_2O + O_2 \end{array}$$

Reaction intermediate is used up in the second step

We know that Cl is an intermediate because it is made and then used up before the end of the reaction

2) Find the overall reaction given the steps:

Reaction intermediate

$$\begin{array}{ll} \text{step 1:} & NO + Cl_2 \rightarrow NOCl + \cancel{Cl} \\ \text{step 2:} & \cancel{Cl} + NO \rightarrow NOCl \\ \hline \text{overall:} & 2NO + Cl_2 \rightarrow 2NOCl \end{array}$$

3) Figure out what step 1 is given all other steps and the overall

step 1:

step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

overall: $NO_2 + CO \rightarrow NO + CO_2$

NO_3 is NOT a reactant in the overall reaction therefore it is a reaction intermediate (made in step 1)

NO is not made in step 2 therefore it is made in step 1

NO_2 has not been used in step 2, but it is formed in step 2 therefore $2NO_2$ molecules are used in step 1

$$\begin{array}{ll} \text{step 1:} & \cancel{NO_2} + NO_2 \rightarrow NO + \cancel{NO_3} \\ \text{step 2:} & \cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2 \\ \hline \text{overall:} & NO_2 + CO \rightarrow NO + CO_2 \end{array}$$

Note: this reaction is an example of autocatalysis because some of the reactant is used and then reproduced which means some of the reactant is behaving as a catalyst

Therefore step 1 is $2NO_2 \rightarrow NO + NO_3$

4) Catalysts and Reaction Mechanism

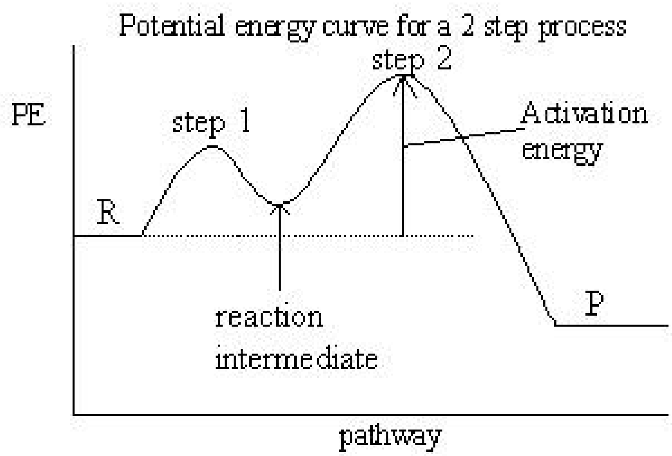
catalyst used up

$$\begin{array}{ll} \text{step 1:} & H_2O_2 + I^- \rightarrow H_2O + IO^- \\ \text{step 2:} & IO^- + H_2O_2 \rightarrow H_2O + I^- + O_2 \\ \hline \text{overall:} & 2H_2O_2 \rightarrow 2H_2O + O_2 \end{array}$$

catalyst re-formed

PE diagrams and Mechanisms

Potential energy diagrams for multiple step reactions will have a hill for each step of the reaction. The activation energy for the reaction is from the reactants to the top of the highest hill.

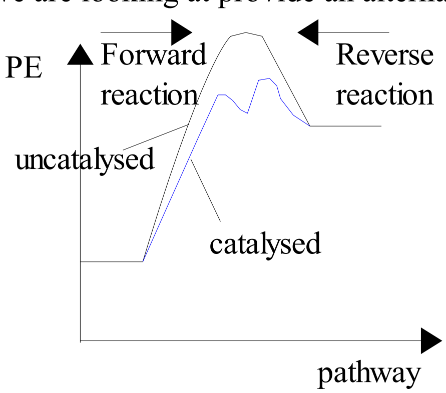


What you are expected to be able to do in a reaction mechanism question:

1) Identify reaction intermediates (starts **ri**ght and ends left)
2) Identify the catalyst (starts left and ends right)
3) Figure out the OVERALL reaction given all the steps
4) Figure out a missing step from the overall and the other steps
5) State whether a given mechanism is likely – are all the steps 2 particle collisions?

VI. Catalysis

A catalyst increases the rate of a reaction without being consumed in the reaction. Most of the catalysts we are looking at provide an alternate mechanism with a lower activation energy.



Notice that although the activation energy is lower the value of ΔH does not change. This is because ΔH is due to the energy of the reactants and products, and the reactants and products do not change in the overall reaction.

A catalyst will not produce more product, it will only allow you to produce the product faster than the uncatalysed reaction.

When a catalyst is used the FORWARD and REVERSE reaction rates both increase. More about this in the next unit.

Inhibitors

Inhibitors don't affect the shape of the PE diagram because they don't get involved in the mechanism. Inhibitors work by sticking to the active sites on reactants. This decreases the concentration of usable reactant.

Industrial Catalysts (for interest – not on test!)

- a wide variety of catalysts are used
- many are transition metals Pt, Pd, Rh, Ni, Cu, Fe
- more expensive metals are coated on high surface area clays which have a honeycomb or sponge like structure.
- Rayney Nickel
  - very common
  - alloy of Ni and Al is washed out with NaOH leaving Ni with a spongey structure
- some industrial catalysts don't get involved in the mechanism instead they act by trapping the reactants with a particular geometry so that the collisions can be more successful.