REACTION KINETICS

VISUAL CHEM CARDS

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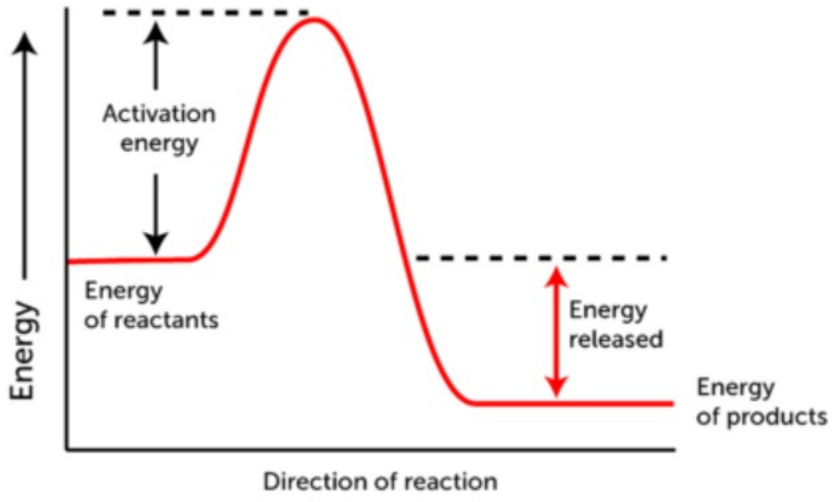
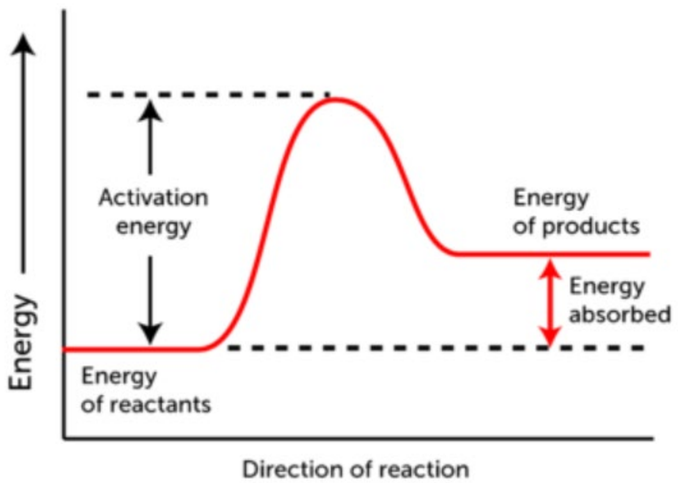
Reaction Energy Profiles

Reactants $\rightarrow$ Products

EXOTHERMIC REACTION





Activation energy (E_A) - minimum energy needed by particles when they collide for a reaction to occur.

Breaking & Forming Bonds

Reactants → Products

In a chemical reaction, bonds between atoms in the reactants are broken, and atoms rearrange and form new bonds to make the products.

	Bond Breaking	Bond Formation
Type of process	Endothermic	Exothermic
Heat energy transfer	Taken in	Given out

Energy is transferred when bonds are broken or are formed.

During a chemical reaction:
- bonds in the reactants are broken
- new bonds are made in the products

The difference between the energy needed to break bonds and the energy released when new bonds are made determines the type of reaction.
- is released in making bonds in the products than is taken in when breaking bonds in the reactants
- endothermic if less heat energy is released in making bonds in the products than is taken in when breaking bonds in the reactants.

Hydrogen and chlorine react to form hydrogen chloride gas:

$$H{-}H + Cl{-}Cl \rightarrow 2H{-}Cl$$

Bond	Bond energy
H−H	436 kJ mol^{-1}
Cl−Cl	243 kJ mol^{-1}
H−Cl	432 kJ mol^{-1}

Energy in = 436 + 243 = 679 kJ mol^{-1}

Energy out = (2 × 432) = 864 kJ mol^{-1}

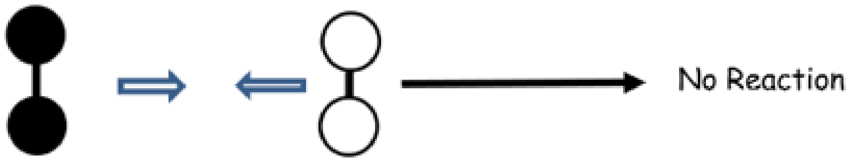
Energy change = in - out

= 679 - 864

= -185 kJ mol^{-}

Collision Theory

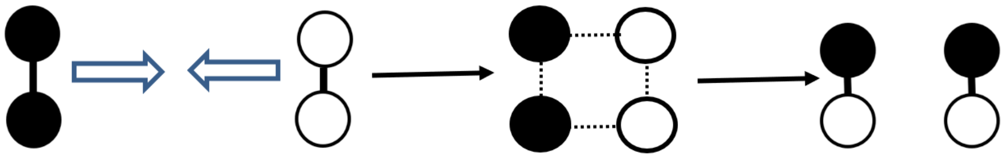
Collision Theory - reactants must collide in order to react and form products. Only effective collisions of the correct orientation and sufficient energy to over the barrier to reaction (E_A) will result in a reaction.



Correct orientation of collision. Insufficient energy of collision to overcome the activation energy (E_A). No reaction.

Energy of collision > activation energy (E_A).

Incorrect orientation of collision. **No reaction.**



Energy of collision > activation energy (E_A).

Correct orientation of collision. **Reaction takes place.**

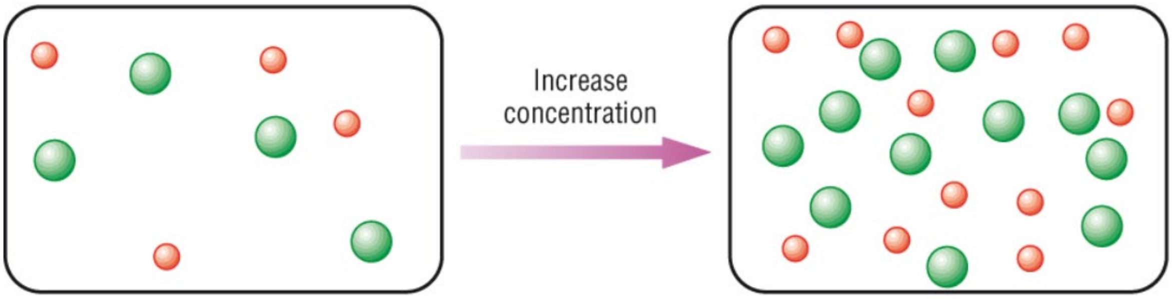
Rates of Reaction

Rate of Reaction = [Change in Concentration]/Time

Rate of reaction can be increased by increasing the number of effective collisions, i.e.

- increasing reactant concentration
- increasing reaction temperature
- increasing pressure (gaseous reactants)
- surface area of reactants
- and the presence of catalysts

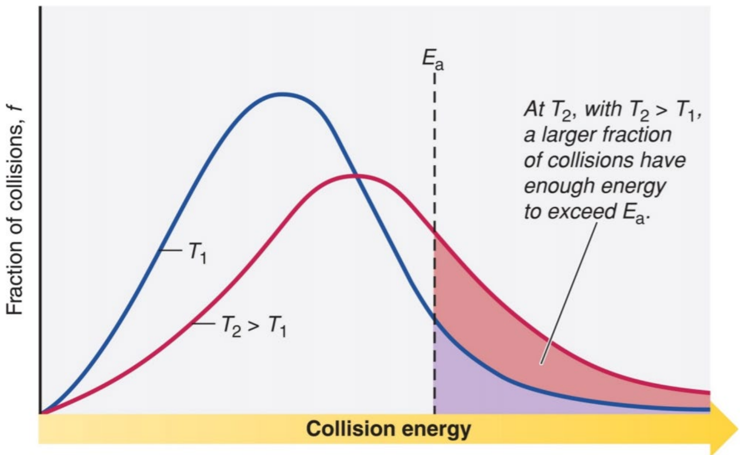
Increasing Concentration



Few molecules
Few collisions
Low rate of reaction

Many more molecules
More collisions
Higher rate of reaction

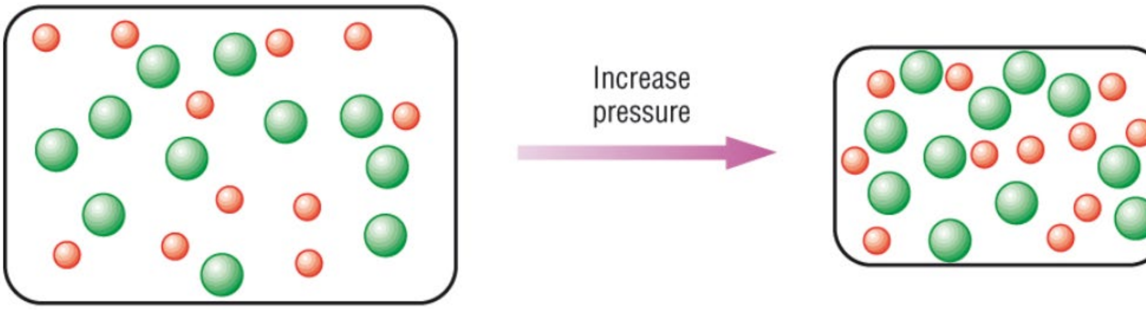
Increasing Temperature



As Temperature increases, more collisions will take place and more will have energy greater than E_A

Rates of Reaction

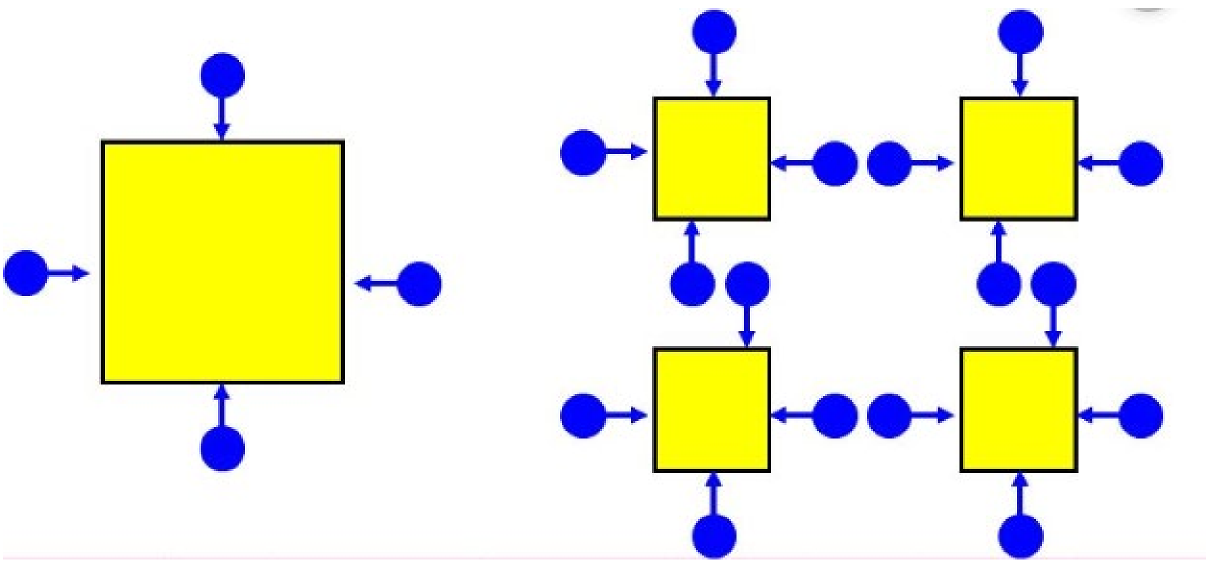
Increasing Pressure



Molecules have lots of space – few collisions
Low rate of reaction

Molecules have space to move and are more likely to collide.
Higher rate of reaction

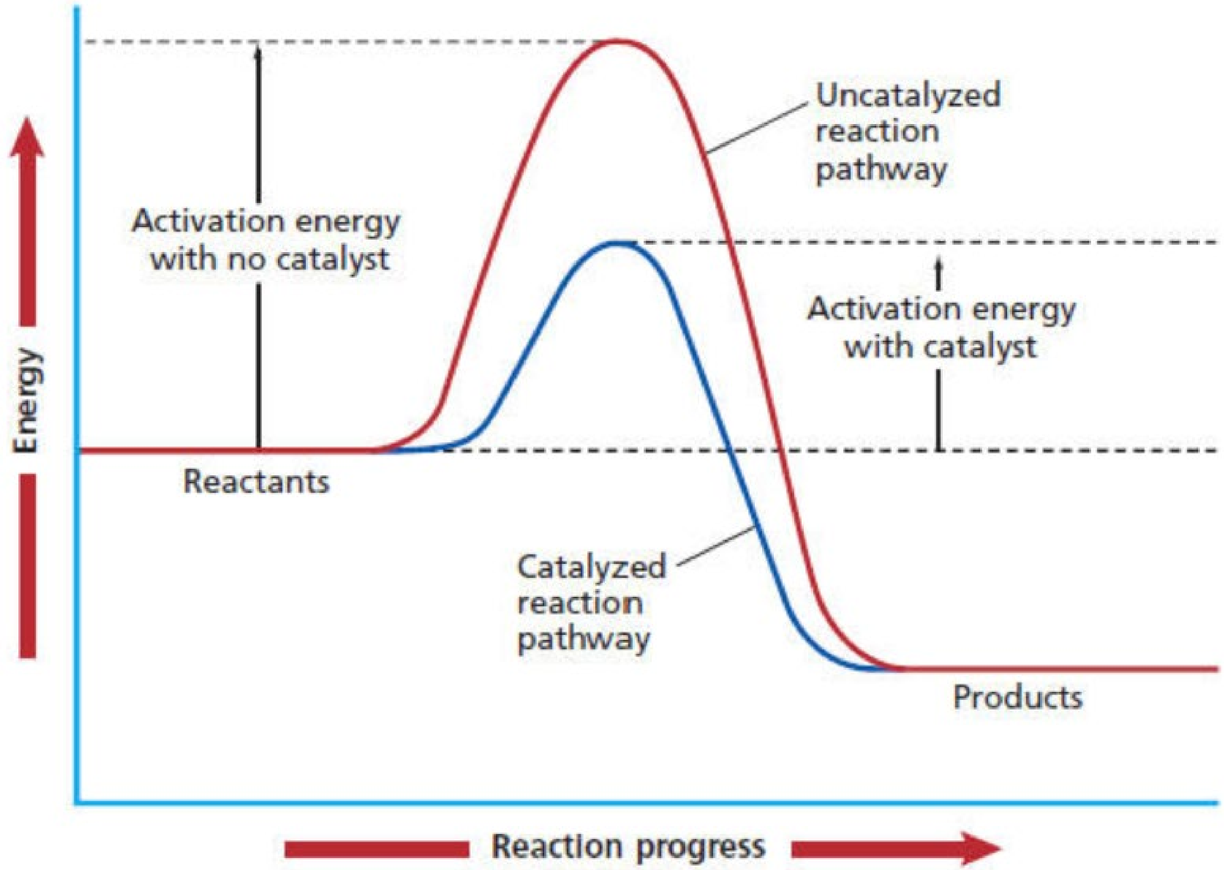
Increasing Surface Area/Decreasing Particle Size



The smaller the particle size - the greater the surface area – the greater the number of collisions – the greater the rate of reaction.

Rates of Reaction

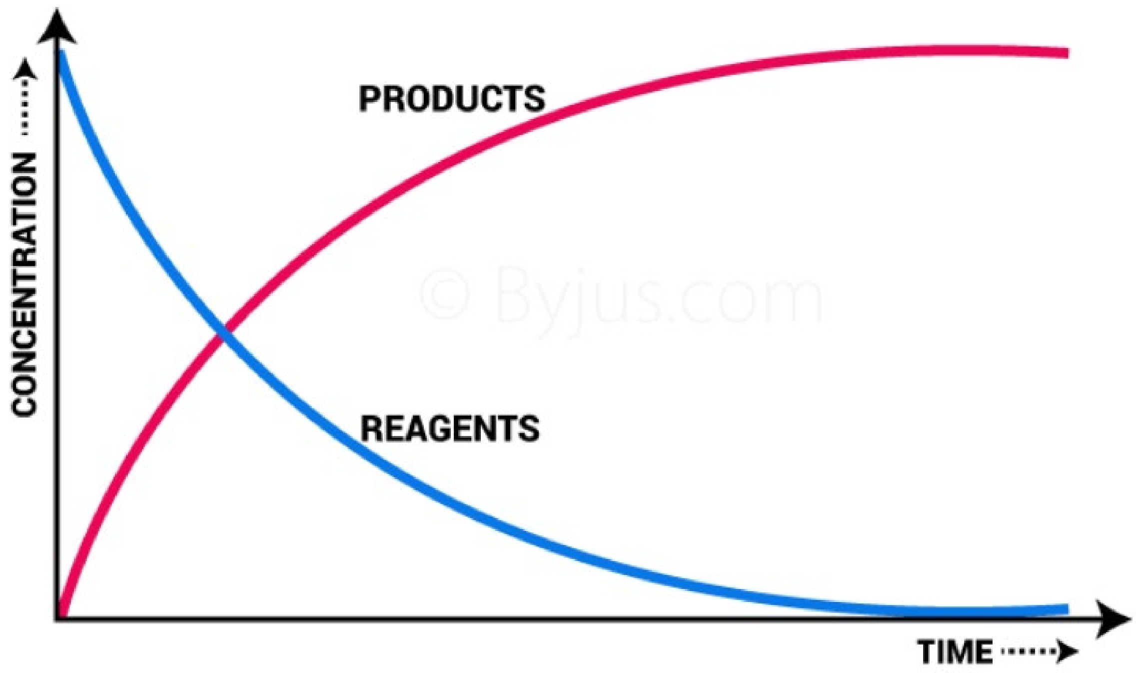
Effect of catalyst on reaction rate



A catalyst speeds up a chemical reaction, without being consumed by the reaction.

Catalysts increase the reaction rate by lowering the activation energy for a reaction

Rates of Reaction



When a reaction starts the concentrations of the reactants are at their highest, the rate is at its fastest.

As the reactants are used up the concentration decreases, so does the rate.

When one of the reactants is used up the reaction stops

Rates of Reaction

$$aA + bB + \ldots \longrightarrow cC + dD + \ldots$$

Order of reaction with respect to **A.**

Order of reaction with respect to **B**.

$$\text{Rate} = k[A]^a\,[B]^b$$

Rate constant

Concentrations in mol dm^{-3}

k is specific for a given reaction at a given temperature.

Reaction orders ‘a’ and ‘b’ are determined experimentally.

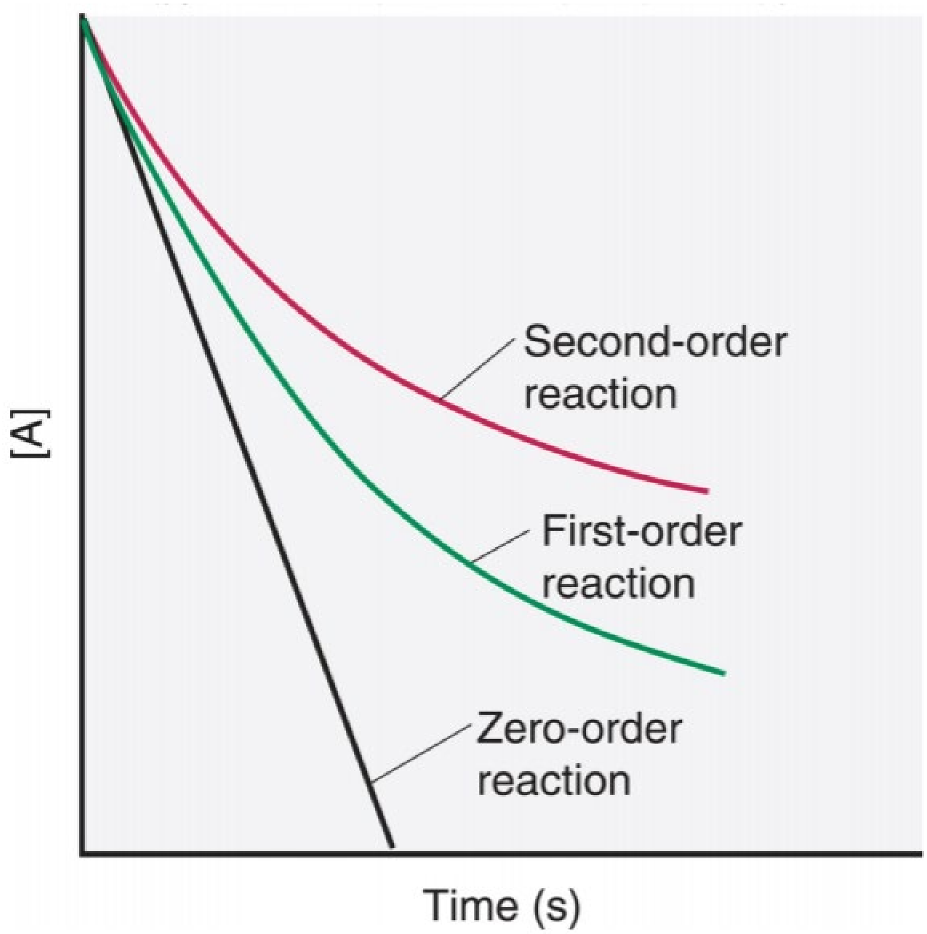
A reaction has an individual order “with respect to” or “in” each reactant.

For the simple reaction A → products: If the rate doubles when [A] doubles, the rate depends on $[A]^1$ and the reaction is **first order** with respect to A.

If the rate quadruples when [A] doubles, the rate depends on $[A]^2$ and the reaction is **second order** with respect to [A].

If the rate does not change when [A] doubles, the rate does not depend on [A], and the reaction is **zero order** with respect to A.

Orders of Reaction



Example: $NO_{(g)} + 2H_{2(g)} \longrightarrow N_{2(g)} + 2H_2O_{(g)}$

$$rate = k[NO]^2[H_2]$$

The reaction is **second order** with respect to NO, **first order** with respect to H_2 and **third order overall.**

Reaction orders must be determined from experimental data and cannot be deduced from the balanced equation.

Orders of Reaction

An integrated rate law includes ***time*** as a variable.

First-order rate equation:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]$$

$$\boxed{\ln\frac{[A]_0}{[A]_t} = kt}$$

Second-order rate equation:

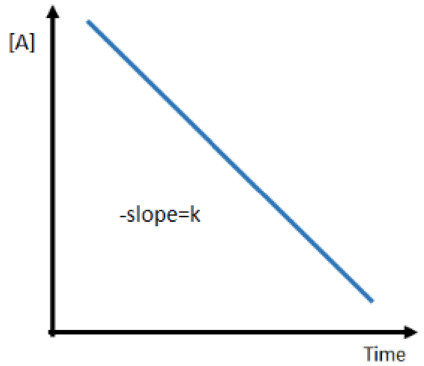
$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]^2$$

$$\boxed{\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt}$$

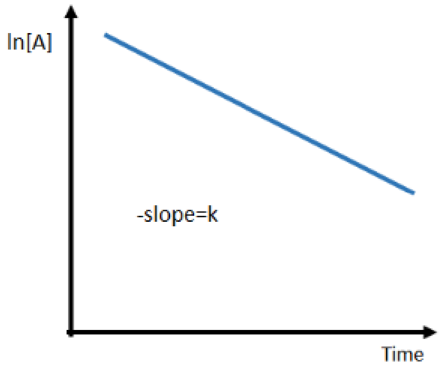
Zero-order rate equation:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]^0$$

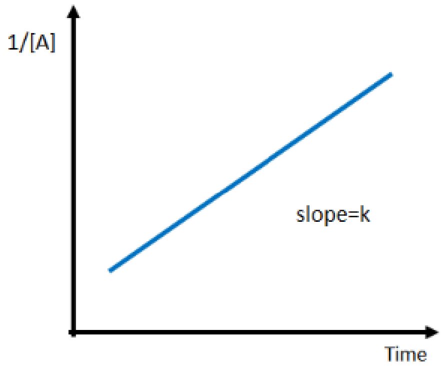
$$\boxed{[A]_t - [A]_0 = -kt}$$



Zeroth-order Reaction



First-order Reaction



Second-order Reaction

Temperature & the Rate Constant

Arrhenius Equation

$$k = A\, e^{-E_A/RT}$$

k = rate constant

A = frequency factor

E_A = activation energy

k increases exponentially with temperature

Temperature has a dramatic effect on reaction rate. In many reactions, a 10°C increase will double or even triple the rate.

Higher T $\longrightarrow$ **Larger k** $\longrightarrow$ **Increased Rate**

Activation Energy

In order to be ***effective***, collisions between particles must exceed a certain energy ***threshold***.

When particles collide effectively, they reach an ***activated state***. The energy difference between the reactants and the activated state is the ***activation energy*** (***E_a***) for the reaction.

The ***lower*** the activation energy, the ***faster*** the reaction.

Smaller E_a → larger f → larger k → increased rate