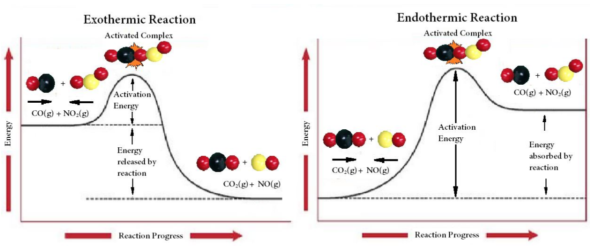
12.5 - 12.7 - Mechanisms & Calatysts



Reaction Mechanisms

Most chemical reactions occurring via a series of steps called a reaction mechanism - because reactions are generally much more complex than a balanced reaction would suggest.

As the reaction mechanism proceeds, a sequence of reactions can be parsed into discreet elementary steps (components of the mechanism) occurring at different relative rates.

Chemicals that are formed, then consumed during a reaction are called intermediates.

A chemical that accelerates a reaction (or allows it to happen at all), but is not consumed during the reaction is called a catalyst.

More Terms

Molecularity: the number of species that must collide to produce a reaction.
Probability drives molecular orientation, speed, angle as particles collide and interact.

Depending on how many species are involved with a collision, words describe the increasingly complex interactions between individual components:
unimolecular: one molecule breaking apart;
bimoecular: two species colliding;
termolecular: three species colliding. These are rare.

Elementary Steps Table

Elementary Step	Moleculality	Rate Law
A --> products	Unimolecular	Rate = k[A]
A + A --> products (2A --> products)	Bimolecular	Rate = $k[A]^2$
A + B --> products	Bimolecular	Rate = k[A][B]
A + A + B --> products (2A + B --> products)	Termolecular	Rate = $k[A]^2[B]$
A + B + C --> products	Termolecular	Rate = k[A][B][C]

Two constraints upon a reaction mechanism are:
1. The sum of the elementary steps must give the overall balanced equation fot the reaction.

2. The mechanism must agree with the experimentally determined rate law.

Guided Mechanism Example

Consider the reaction between nitrogen dioxide and carbon monoxide. knowing that it produces nitrogen monoxide and carbon dioxide doesn't tell the whole detail of the reaction.

1. If the rate law is known to be $k[NO_2]^2$, what is the net reaction from the following two steps?

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{k_1} NO_{3(g)} + NO_{(g)}$$
$$NO_{3(g)} + CO_{(g)} \xrightarrow{k_2} NO_{2(g)} + CO_{2(g)}$$

Note: k_1 and k_2 are the rate constants of the individual steps.

2. What is the reaction intermediate?
3. What is the rate law for the reaction?

Guided Mechanism Answers

1. By crossing out identical species in reactants and procucte, the net chemical reaction becomes:

$$\cancel{NO_{2(g)}} + NO_{2(g)} \xrightarrow{k_1} \cancel{NO_{3(g)}} + NO_{(g)}$$
$$\cancel{NO_{3(g)}} + CO_{(g)} \xrightarrow{k_2} \cancel{NO_{2(g)}} + CO_{2(g)}$$

$$NO_{2(g)} + CO_{(g)} \xrightarrow{k} CO_{2(g)} + NO_{(g)}$$

2. The reaction intermediary is nitrogen trioxide (NO_3), a radical that forms and is resorbed as the reaction proceeds. It is a free radical - a species with an odd number of electrons (very reactive).

Guided Mechanism Answers

3. The the rate law for the reaction involves each of the two species in the reaction. Because the nitrogen dioxide self reacts in the first step, it is second-order:

Rate = k$[A]^2[B]$

Rate-Determining Step

Multistep reactions often have one step that is slower than the others: reactants become products only as fast as they get through this slowest step.

In our previous example, if the first reaction is the slow one (and thus rate-determining), and the second is slower, it is the rate of the first reaction that will set the overall rate.

$NO_{2(g)} + NO_{2(g)} \longrightarrow NO_{3(g)} + NO_{(g)}$ slow

$NO_{3(g)} + CO_{(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$ fast

The rate limiting step's rate:

$$Rate\ NO_3\ formation = \frac{\Delta[NO_{3]}}{\Delta t} = k_1[NO_2]^2$$

Using our earlier rate law, and since the overall reaction rate can be no faster than the slowest step:

Overall rate = $k_1[NO_2]^2$

Reaction Rate vs. Temperature

The speed of most chemical reactions increases with an increase in temperature.

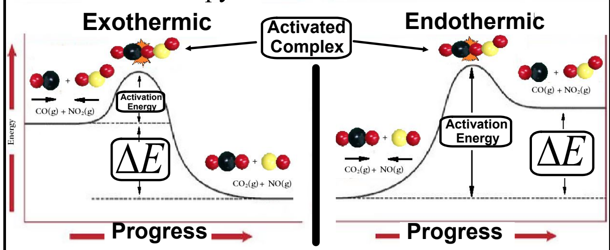
The collision model of chemical kinetics states that molecules must collide to interact (with correct orientation, speed, etc.).

At an increased temperature, as molecules speed up, their collision rate increases, thus increasing their probability of reacting. Also, at higher temperatures, faster moving molecules can collide with more energy, allowing bonds to be broken so that new ones can form.

At a certain threshold energy, called the activation energy (E_a), molecules are moving fast enough to achieve this. This environment of reacting molecules is called the activated complex, or transition state.

Graphical Summary of Activation Energy.

A common analogy of activation energy is that of a hill which reactants must climb, and once over, products descend.
If the reaction is exothermic, products will have less enthalpy than reactants; if endothermic, they will have more enthalpy.



Reaction Rate Math

Svante Arrhenius posited in the 1880's that since temperature vastly increases collision rate (and energy), it must factor in a calculation.
His theory is:
Number collisions with E_a = (total collisions)$e^{-Ea/RT}$

Since molecular orientations factor in, a rate constant expression is: $k = zpe^{-Ea/RT}$
where z = collision frequency and p is called the steric factor and reflects the fraction of collisions with effective orientations.

The Arrhenius Equation is:

$$k = Ae^{-E_a/RT}$$

A = frequency factor
E_a = activation energy (J)
R = Universal Gas Constant (8.31 J/K mol)
T = Temperature (K)

More Math

Manipulating the equation gives:

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

If a plot of ln(k) vs. 1/T yields a linear relation, then the reaction's rate constant obeys the Arrhenius equation and can be used to solve reaction parameters (this equation is y = mx + b).
Most reactions obey this equation, so the collision model is reasonable.

Another way to determine activation energy relies on finding rates at different temperatures:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Catalysis

A catalyst is a substance that speeds up a reaction without being consumed itself.

Some catalysts allow a reaction to happen at a lower than normal temperature by providing an additional pathway for a reaction to proceed - one with a lower activation energy.

Homogeneous catalyst: one in the same phase as the reactants.

Heterogeneous catalyst: one in a different phase, usually a solid.

Demo: MnO_2 powder in H_2O_2

4. Balance the reaction:
hydrogen peroxide decomposes into water and oxygen in the presence of manganese (IV) oxide.
Hint: a catalyst is usually written above the arrow,

$$\xrightarrow{MnO_2}$$

5. Observe the demonstration then record your observations both during the reaction and during the oxygen test.

Applications

Catalysts have a wide application in chemistry.

Enzymes in our bodies allow for reactions to occur below temperatures that would damage the cells hosting the reactions.

Catalytic converters in automobiles allow for more thorough combustion of hydrocarbons, diminishing nitrogen oxides and carbon monoxide.

Homework

Read 12.5 in your Textbook

12.4.B Problems in your Booklet
Due Next Class