13.5 REACTION MECHANISMS

Many chemical reactions occur by a sequence of 2 or more steps – the specific sequence of steps is referred to as the reaction mechanism.

Each individual event in the overall reaction is called an **elementary step**.

Molecularity: number of molecules that react in an elementary step

Unimolecular: 1 molecule $A \rightarrow$ products

Bimolecular: 2 molecules $2A \rightarrow$ products or $A + B \rightarrow$ products

Termolecular (uncommon): $3A \rightarrow$ products or $2A + B \rightarrow P$ or $A + B + C \rightarrow P$

Example. The 2 step mechanism for the overall reaction $Br_2 + 2NO \rightarrow 2BrNO$ is:

Step 1: $Br_2 + NO \rightarrow Br_2NO$ (Bimolecular step)

Step 2: $Br_2NO + NO \rightarrow 2BrNO$ (Bimolecular step)

Intermediates are short lived species that are formed during the reaction, then are subsequently consumed. Intermediates do not appear in the overall balanced equation. e.g. Br_2NO for the example above

$\Rightarrow$ For an elementary step, the rate law can be written using the stoichiometric coefficients of the reactants (molecularity = order).

E.g. Step 1 in the reaction above: Rate =

Rate determining step: the slowest step in the reaction is the rate determining step; this step limits how fast products can form. Analogy: freeway during rush hour

$\Rightarrow$ The rate law for the overall reaction is determined by the rate of this step.

Mechanisms with an Initial Slow Step

Example. The mechanism for the overall reaction $2NO_2 + F_2 \rightarrow 2NO_2F$ is proposed to be:

Step 1: $NO_2 + F_2 \rightarrow NO_2F + F$ (slow)

Step 2: $F + NO_2 \rightarrow NO_2F$ (fast)

What is the Rate Law for this reaction? **Rate =**

$\Rightarrow$ The reactants for the slow step (step 1) give us the rate law for the overall reaction.

Mechanisms with an Initial Fast Equilibrium Step

Many chemical reactions involve mechanisms with equilibrium steps:

Example. The mechanism for the reaction $Br_2 + 2NO \rightarrow 2BrNO$ occurs via two steps:

Step 1: $Br_2 + NO \rightleftarrows Br_2NO$ (fast equilibrium)

Step 2: $Br_2NO + NO \rightarrow 2BrNO$ (slow)

What is the Rate Law predicted by this mechanism?

$\Rightarrow$ From the slow step: Rate =

$\Rightarrow$ However, it is not possible to accurately measure the concentration of an intermediate so an intermediate cannot be part of an experimental rate law.

$\Rightarrow$ Since most of Br_2NO decomposes during the equilibrium reaction established in step 1, we can set up an equilibrium expression based on the rates of the forward and reverse reactions:

Rate of forward reaction = Rate of reverse reaction

$\Rightarrow$ Solve for [intermediate]:

$\Rightarrow$ Substitute in Rate law:

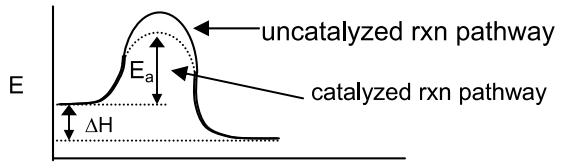
Experimentally you should observe the rate law: **Rate = k[NO]^2[Br$_2$]** where k = $k_2 \frac{k_1}{k_{-1}}$ (k is the experimentally obtained rate constant)

13.6 CATALYSIS

Catalyst: A substance that increases the rate of reaction, but is not part of the overall reaction.

- A catalyst lowers the E_a $\Rightarrow$ usually a catalyst helps weaken or break reactant bonds.
- A catalyst alters the reaction mechanism, but does not change the overall reaction.
- A catalyst may appear in the experimental rate law $\Rightarrow$ a reaction may have more than one rate law.

Catalyzed reaction: E_a is lower, but ΔH = ΔH (products) - ΔH (reactants) is the same:



Heterogeneous – The catalyst is in a different phase than the reactants. Typically, a metal is used to provide a surface upon which reactants can adsorb and react.

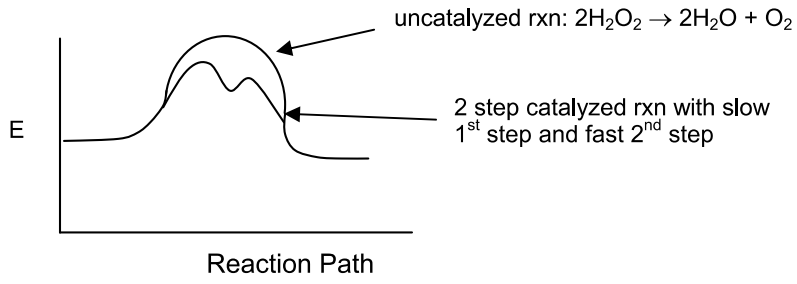
E.g. Catalytic converters contain platinum metal mixed with rhodium. Pt catalyzes the oxidation of CO and unburned hydrocarbons to CO_2 and H_2O. Rh converts NO to N_2 and O_2.

Homogeneous – The catalyst is in the same phase as the reactants. The catalyst is consumed, then regenerated in a subsequent step. Homogeneous catalyst may appear in rate law.

Example. Homogeneous catalyzed decomposition of hydrogen peroxide: $2H_2O_2 \rightarrow 2H_2O + O_2$

Step 1 $H_2O_2 + I^- \rightarrow H_2O + IO^-$ Slow

Step 2 $H_2O_2 + IO^- \rightarrow O_2 + H_2O + I^-$ Fast



Enzymes - Large protein molecules with one or more active sites that serve as biological catalysts in living organisms. The enzymes are compatible with specific substrate molecules.