Mechanism Concept

1) Exponents in rate law do not depend on stoichiometric coefficients in chemical reactions.

2) What is the detailed way in which the reactants are converted into products? This is not described by the chemical equation, which just accounts for mass balance.

3) Rate at which reaction proceeds and equilibrium is achieved, depends on the **Mechanism** by which reactants form products.

Elementary Reactions: these are hypothetical constructs, or our guess about how reactants are converted to products.

The **Mechanism** is a **set** of **Elementary Reactions**!

suppose reaction actually takes place during a collision of H_2 with Cl_2 (this is the binary collision picture):
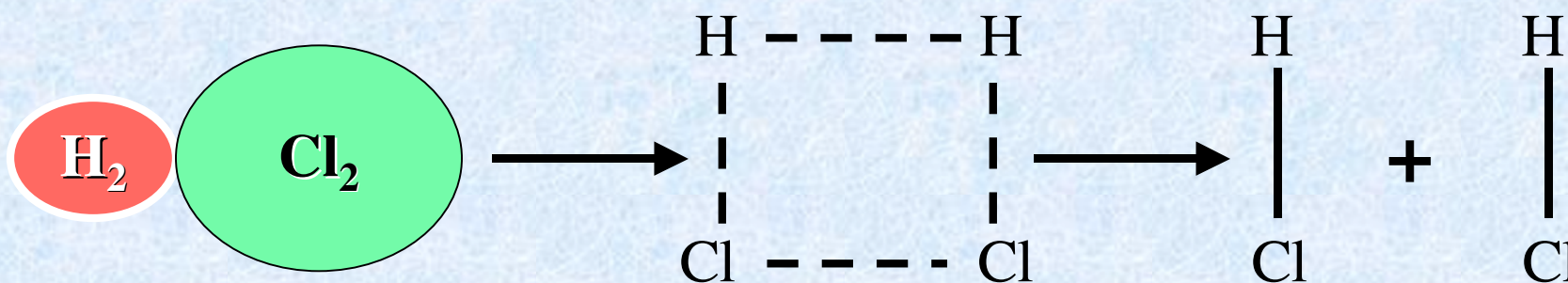
The above is a __bimolecular__ elementary reaction.
 A unimolecular elementary reaction might be

$HO_2 \rightarrow H + O_2$

HO_2 just dissociates without any other influence.

Rate Laws for Elementary Reactions:

1) A $\rightarrow$ Fragments, depends only on A (No collisions)

2) A+A $\rightarrow$ Products, depends only on A, A collision

A + B → Products.

Elementary reaction is one place where stoichiometry and rate <u>are</u> related. However never know when you have an elementary reaction. Must guess and then verify with experiment. Elementary reactions are hypothetical constructs!

Unimolecular Decompositions

An example of
Mechanisms, Steady State Approximation,
and Elementary Reactions

A → Fragments

pyrazine → 2HCN + HC≡CH (Δ)
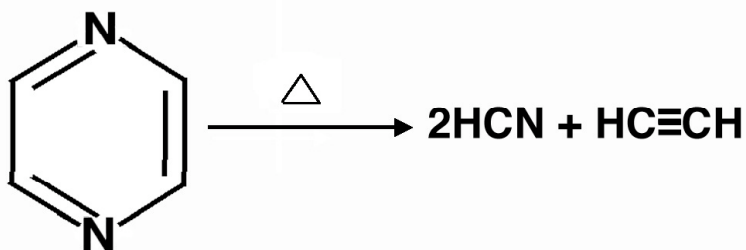
Observed Experimentally to
be first order in pyrazine.

$$-\frac{dA}{dt} = k[A] \quad \text{or} \quad C \text{ - } B \rightarrow C + B \text{ with}$$

Lindemann [Lord Cherwell] suggested the following mechanism:

Assume, however, that after A* is produced by a collision it hangs around for some time before decomposing. This time lag between activation and reaction may be thought of as the time necessary to transfer energy among the internal (vibrational) coordinates.

If A^* exists for a reasonable time it could suffer a collision and drop down to a lower energy where it cannot decompose.

Collision between $A(E_1)$ and $A(E_2)$ creates "activated" $A^*(E^*)$

E_1, E_2, $E_3 < E_{min}$; $E^* \geq E_{min}$ = energy necessary for decomposition

Competition between reaction of $A^*(E^*)$ to form products and collisional cooling of $A^*(E^*)$ to produce unreactive $A(E_5)$ and $A(E_6)$

Again E_4, E_5, $E_6 < E_{min}$ (k_1, k_{-1}, and k_2 are kinetic rate constants)

k_2 is decomposition step assumed irreversible.

Mechanism Elementary Steps:

$$A + A \xrightarrow{\quad k_1 \quad} A^* + A \qquad \text{Step 1}$$

$$A^* + A \xrightarrow{\quad k_{-1} \quad} A + A \qquad \text{Step 2}$$

$$A^* \xrightarrow{\quad k_2 \quad} P \qquad \text{Step 3}$$

$$\frac{dP}{dt} = k_2[A^*]$$

Don't know what $[A^*]$ is, however the number of $[A^*]$ must be small or the reaction would go to completion very quickly. A* is a "bottleneck" for the reaction since product is only formed via A*.

$$d[A^*]/dt = 0 = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$$

The **Steady State** Approximation

Solve for $[A^*]$ →

Steady state approach allows us to solve for concentration of unknown species $[A^*]$ in terms of known $[A]$ concentration.

Fundamental result of Lindemann "Unimolecular Reaction Mechanism"

Note, multistep mechanism leads to complex rate expression!

Two Limiting Cases

I)

$$\text{Rate} = \frac{dP}{dt} = k_2[A^*] = \frac{k_2 k_1 [A]^2}{k_2 + k_{-1}[A]}$$

This says the rate of decomposition of A^* is much <u>faster</u> than the rate of deactivation.

Thus, $dP/dt \cong k_1[A]^2$ }2nd order in [A]

At this point, it looks like Mr. Lindemann will have to hand in his Theorists' Club ID card since his scheme seems to predict a second order kinetic dependence on $[A]^2$!

"Physical Interpretation" of this particular limit:

$$k_2 >> k_{-1}[A]$$

Mechanism Elementary Steps:

$$A + A \xrightarrow{\quad k_1 \quad} A^* + A \qquad \text{Step 1}$$

$$A^* + A \xrightarrow{\quad k_{-1} \quad} A + A \qquad \text{Step 2}$$

$$A^* \xrightarrow{\quad k_2 \quad} P \qquad \text{Step 3}$$

Reaction rate here is just the rate at which [A*] is formed since every A* formed falls apart to product P immediately. The rate of formation of A* is obtained from the first step: $d[A^*]/dt = k_1[A]^2$ So the reaction becomes a simple binary collison model, second order process in this limit.

(Case II)

$$\text{Rate} = \frac{dP}{dt} = k_2[A^*] = \frac{k_2k_1[A]^2}{k_2 + k_{-1}[A]}$$

This says there is an appreciable time lag between activation and reaction. Thus, a large amount of <u>deactivation</u> occurs.

Note that $k_{-1}[A]$ is pressure dependent. Gets larger as pressure increases $\{P_A = (n_A/V)RT = [A]RT\}$. Thus, $k_{-1}[A] \gg k_2$ is a good approxmation at high pressures.

$$\frac{dP}{dt} \cong \frac{k_2k_1}{k_{-1}}[A] \Bigg\}$$ **1st order in A (apparent)**

[More careful investigation of "unimolecular" decomp. showed 2nd order kinetics at low pressure.]

"Physical Interpretation" of this particular limit:

$$k_2 << k_{-1}[A]$$

Mechanism Elementary Steps:

$$A + A \xrightarrow{\ k_1\ } A^* + A$$ **Step 1**

$$A^* + A \xrightarrow{\ k_{-1}\ } A + A$$ **Step 2**

$$A^* \xrightarrow{\ k_2\ } P$$ **Step 3**

Reaction rate here is $dP/dt = k_2 [A^*]$ but the concentration of A^* is given by the "equilibrium" condition, $k_{-1}[A^*][A] = k_1[A]^2$. So, solving for $[A^*]$ gives:

Result is that $[A^*]$ scales linearly with $[A]$ and rate, $dP/dt = k_2[A^*]$ also scales linearly with $[A]$.