<u>REACTION MECHANISMS</u>

- In order for a reaction to take place, the reactant particles must collide
- A simultaneous collision of four or more reactant particles is extremely unlikely therefore scientists believe most chemical reactions occur as a sequence of ***elementary steps*** (steps that only involve 1, 2 or 3 particle collisions)
  - The term ***molecularity*** refers to the number of reactant particles that are involved in an elementary step
  - A ***unimolecular*** elementary reaction occurs when one particle reacts
  - A ***bimolecular*** elementary reaction occurs when two particles collide and react
  - A ***trimolecular*** elementary reaction occurs when three particles collide and react
- This series of steps is called a ***reaction mechanism***

- Consider the following reaction: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
  - The odds of these 3 molecules colliding all at once is very rare
  - This reaction actually takes place as a 2-step reaction:
    Step 1: $NO(g) + O_2(g) \rightarrow NO_3(g)$
    Step 2: $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$
  - When you add up the 2 steps, you get the overall reaction
  - $NO_3(g)$ is called a ***reaction intermediate*** (a substance formed in an elementary step but is consumed in another step)

- The slowest elementary step in any reaction mechanism is called the ***rate determining step***
- This step will have the largest activation energy (Ea)
- This step determines the rate of the entire reaction
  - A worker on an assembly line who controls the overall rate of car production doesn't have to be the 1st or last worker but the slowest worker
  - If the slowest worker is at the beginning of the line, other workers will have to wait for cars to arrive at their station
  - If the slowest worker is at the end of the line, partially assembled cars will stack up waiting to be finished
  - Adding workers at the fast steps will have no effect on car production

- Increasing the “concentration” of workers at the slow step will increase car production

- Rate determining steps can occur anywhere in a reaction mechanism however if the slow step is not the first step of the mechanism, the overall rate law is more complicated to determine

Eg)Step 1: $HBr(g) + O_2(g) \rightarrow HOOBr(g)$ (slow)
Step 2: $HOOBr(g) + HBr(g) \rightarrow 2HOBr(g)$ (fast)
Step 3: $HOBr(g) + HBr(g) \rightarrow H_2O(g) + Br_2(g)$ (fast)
$\underline{HOBr(g) + HBr(g) \rightarrow H_2O(g) + Br_2(g)}$
$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$

Rate = k[HBr] [O_2] since this step determines the overall rate, none of the other compounds influences the overall rate of reaction

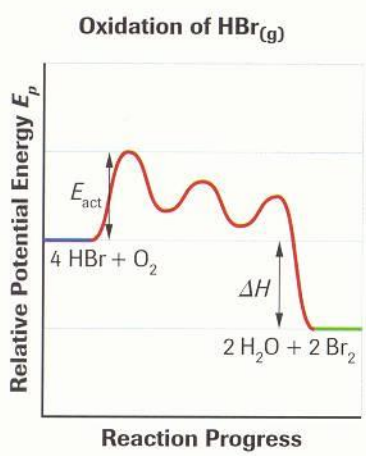

Figure 8
Over the progress of this reaction, the potential energy increase necessary to reach the first activated complex stage is the greatest increase required, so this is the rate-determining (slowest) step. Energy released as kinetic energy past this point is sufficient to quickly carry the reaction mechanism to completion.

- When proposing a “best guess” reaction mechanism:
  i) each step must be elementary and reasonable
  ii) the rate determining step must support the experimentally determined rate law
  iii) the elementary steps must add up to the overall reaction

- we’ve already learned that the rate law cannot be determined by just looking at the overall reaction; it must be determined experimentally
- elementary reactions are an exception
- for an elementary reaction, the exponents in the rate law are the same as the stoichiometric coefficients for each reactant in the chemical equation

Elementary Reaction	Rate Law
$A \rightarrow$ products	Rate = $k[A]$
$A + B \rightarrow$ products	Rate = $k[A]\,[B]$
$2A \rightarrow$ products	Rate = $k[A]^2$
$2A + B \rightarrow$ products	Rate = $k[A]^2\,[B]$