Reaction Mechanism

- A detailed description of the pathway of a chemical reaction
- Not many reactions occur in a single step
- Usually, a series of steps
  - Each step has an activated complex and a unique E_a
  - The slowest step is the **rate determining step**
    - it controls the rate of the overall reaction

Ex: Overall Reaction

$H_2 + Br_2 \rightarrow 2\ HBr$

Reaction Mechanism

$Br_2 \rightarrow 2\ Br^-$

$Br^- + H_2 \rightarrow HBr + H^+$

$H^+ + Br_2 \rightarrow HBr + Br^-$

Reaction Rate Law

- Expresses the effect of the concentration of each reactant on the rate
- Determined by experiment only
- [ ] = molar concentration

Ex: $2H_2 + 2NO \rightarrow N_2 + 2H_2O$

At constant volume, temp, [NO]:

doubling $[H_2]$, doubles rate **and** tripling $[H_2]$, triples rate

At constant volume, temp, $[H_2]$:

double [NO], 4x rate **and** triple [NO], 9x rate

For this reaction, the rate law is:

$\text{Rate} = k[H_2][NO]^2$

k = rate constant

Ex: $A + B \rightarrow C$

At time = 0

	$[A]_o$	$[B]_o$	Initial rate of formation of C
1	0.20	0.20	2.0×10^{-4} M/min
2	0.20	0.40	8.0×10^{-4}
3	0.40	0.40	1.6×10^{-3}

a) Write the rate law

$\text{Rate} = k[A][B]^2$

b) Calculate the rate constant

2.0×10^{-4} M/min = $k[0.20][0.20]^2$ k = **0.025**

8.0×10^{-4} M/min = $k[0.20][0.40]^2$ k = 0.025

1.6×10^{-3} M/min = $k[0.40][0.40]^2$ k = 0.025

c) If initial concentration of both A and B are 0.30M, what is the rate?

$\text{Rate} = k[A][B]^2$

$= 0.025(0.30)(0.30)^2$

$= 6.8 \times 10^{-4}$ M/min

Reaction Order of a Reactant

- The exponent on the reactant concentration in the rate law
- Ex: According to the previous rate law:

  It is first order in A and second order in B

Overall Reaction Order

- The sum of all the reactant orders
- Ex: The reaction above has an overall reaction order of 3 (that's 1+2)

Ex: Determine the rate law for the reaction A + B → C, given the following data:

$[A]_0$	$[B]_0$	[C] After 10 minutes	Rate of production of C
0.100	0.100	0.015	1.5×10^{-3}
0.200	0.100	0.030	3.0×10^{-3}
0.300	0.100	0.045	4.5×10^{-3}
0.100	0.300	0.045	4.5×10^{-3}

Analysis: Rate is directly proportional to [A] and [B] both.

Rate = k[A][B]

Ex: Determine the rate law for the reaction X + Y → Z + W, given the following data:

$[X]_0$	$[Y]_0$	Rate of production of Z
0.100	0.100	1.5×10^{-3}
0.200	0.100	3.0×10^{-3}
0.100	0.200	6.0×10^{-3}
0.200	0.200	1.2×10^{-2}

Analysis: Rate is directly proportional to [X], but has a squared effect to [Y]

Rate = $k[X][Y]^2$

Ex: $2NO + O_2 \rightarrow 2NO_2$ Rate = $k[NO]^2[O_2]$

At a temperature of 500°C, the rate of production of NO_2 has been found to be 0.010 M/min when the concentration of NO and O_2 are 0.50 M each.

a) What is the value of the specific rate constant at this temp?

$$k = \frac{\text{Rate}}{[NO]^2[O_2]} \quad \frac{0.10\text{M/min}}{(0.050\text{M})^2(0.50\text{M})} = 0.080\text{L}^2/\text{mol}^2\text{min}$$

b) What is the rate of production of NO_2 at 500°C, when the concentration of NO is 0.10M and the concentration of O_2 is 0.30M?

Rate = $k[NO]^2[O_2]$

= $(0.080\text{L}^2/\text{mol}^2\text{min})(0.10\text{M})^2(0.30\text{M})$

= 2.4×10^{-4} mol/Lmin

= 2.4×10^{-4} M/min

Arrhenius Equation

Combines three factors:

- number of particles with E_a or more
- number of collisions per second
- number of collisions with correct orientation

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

- R → constant = 8.314 J/mol K
- T → Kelvin temp
- Ea → activation energy
- A → frequency factor (#collisions/orientation)
- k → rate constant