Rate Law

In studying a chemical reaction, it is important to consider not only the chemical properties of the reactants, but also:

- the conditions under which the reaction occurs
- the mechanism (or steps) by which it takes place
- and the rate at which it occurs.

Rate = $\dfrac{\Delta \text{ concentration of a Reactant or a Product}}{\Delta \text{ time}}$

In general, an **increase** in the concentration of a **reactant** increases the rate of a reaction proportionally.

But this is Chemistry class and not Physics so ... sometimes the rate increases and sometimes it does not when you increase the concentration of a reactant.

Sample Mechanism: cat ⇒ written over the arrow

Step 1	A + B → C (IP)		**fast**
Step 2	C + D → E (IP) + F		**fast**
Step 3	E + G → B + H		**slow**

Overall Reaction: $A + D + G \xrightarrow{B} F + H$

What might happen to the rate of reaction if the concentration of A were increased?

probably no effect bec A is a part of a fast step.

In comparison, what might happen to the rate of reaction if the ↑concentration of G↑ and why?

G is part of the slowest step, the RDS,

so an ↑ in its [ ] should have a major

effect.

The expression called the Rate Law indicates whether or not an increase in a reactant concentration has an effect on the rate and by how much, if any.

The relationship between the **rate of a reaction** and the **concentrations of the reactants** is expressed by a **rate law.**

The general rate law equation is:

rate constant ⇒ specific to the reaction & the temperature at which the rxn is done

$$r = k\,[A]^x\,[B]^y$$

where:

r is the rate law

A and B are reactants in mol/L

x and y are **coefficients** that **indicate how the concentration affects** the rate of reaction

k = rate constant ⇒ # + icky units

For the reaction: **2 A + B → C + D**

If the mechanism of the reaction involves only 1 step (very rare) the **rate law coefficients** are given by **the mole ratios from the BCE**:

$$r = k\,[A]^2\,[B]$$

This assumes **a one step reaction** where all the reactant molecules collide at the same time and are **equally responsible** for the rate of the reaction.

But … usually chemical reactions take place in a **multi-step** fashion.

And not all of the steps in the reaction occur at an equal rate.

Some steps are slow and some steps are fast.

(RDS)

The rate determining step is the slowest step and has the highest activation energy.

For a multi-step reaction, the rate law must be determined experimentally—in the lab by trial. * we will do this as a lab in January Mon & Tues when we get back

1) The rate is first determined with all the reactants at specific concentrations.

2) Then the concentration of one of the reactants is changed and the other reactants' concentrations are held constant and the rate is measured again.

3) Then the concentration of a different reactant is changed and the rate is measured again.

Problem: Determine the rate law for the following reaction:

Given the data below, find the rate law for the following reaction at 300 K and the corresponding rate constant.

$$1A + 1B \rightarrow C + D$$

*If the reaction were to occur in 1 step then the rate law would be:

$r = k[A]^1[B]^1$ from BCE

$r = \frac{2\ L^2}{mol^2 s}[A]^1[B]^2$ from experimental data

But the following data was collected for the reaction:

Trial	$[A]_{initial}$ (M) $\left(\frac{mol}{L}\right)$	$[B]_{initial}$ (M) $\left(\frac{mol}{L}\right)$	$r_{initial}$ (M/sec) $\left(\frac{mol}{L\,s}\right)$
1	1	1	2
2	1	2	8.1
3	2	2	15.9

1) trial 1 → 2 ([A] held constant) 1 → 1

$[B]^x$ = rate

$\left(\frac{2}{1}\right)^x = \frac{8.1}{2}$

$2^x = 4$

$\therefore x = 2$

2) trial 2 → 3 ([B] = constant) 2 → 2

$[A]^y$ = rate

$\left(\frac{2}{1}\right)^y = \frac{15.9}{8.1}$

$2^y = 2$

$\therefore y = 1$

so $r = k[A]^1[B]^2$

3) solving for k

$r = k[A]^1[B]^2$

$\frac{r}{[A]^1[B]^2} = k$

use trial 1 #'s

$\frac{2\frac{mol}{L\,s}}{\left(1\frac{mol}{L}\right)\left(1\frac{mol}{L}\right)^2} = k$

$\frac{2\ L^2}{mol^2 s} = k$