

## Rate Law

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

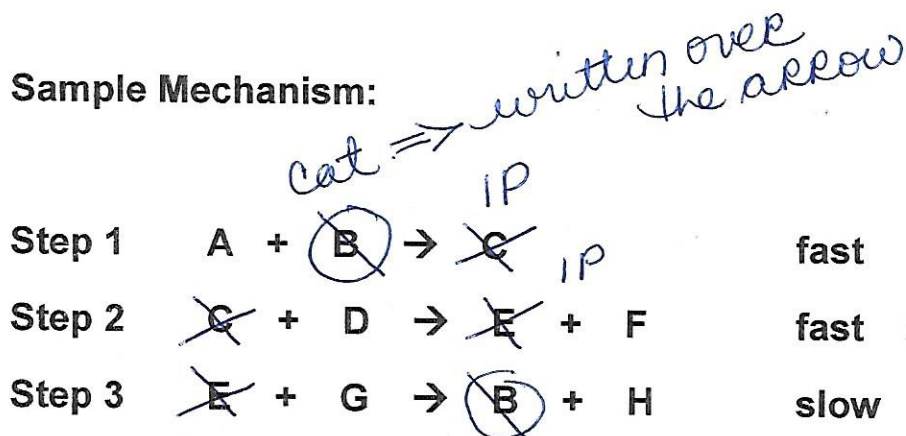
- the conditions under which the reaction occurs
- the mechanism (or steps) by which it takes place
- and the rate at which it occurs.

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

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:



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  $\uparrow$  concentration of G  $\uparrow$  and why?

G is part of the slowest step, the RDS,  
so an  $\uparrow$  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:

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

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  $\Rightarrow$  # & icky units

rate constant  $\Rightarrow$  specific to the reaction & the temperature at which the rxn is done

For the reaction:  $2A + B \rightarrow C + D$

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.

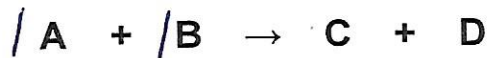
For a multi-step reaction, the rate law must be determined experimentally—in the lab by trial.

*\* 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.



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

$$r = k [A]^1 [B]^1 \text{ from BCE}$$

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

But the following data was collected for the reaction:

Trial	[A] <sub>initial</sub> (M)	[B] <sub>initial</sub> (M)	r <sub>initial</sub> (M/sec)
1	1	1	2
2	1	2	8.1
3	2	2	15.9

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

$$[B]^x = \text{rate}$$

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

$$2^x = 4$$

3) solving for k

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

2) trial 2 → 3  
([B] = constant)  
2 → 2

$$[A]^y = \text{rate}$$

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

$$2^y = 2$$

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

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

$$\frac{(1 \text{ mol})}{4} \left(\frac{1 \text{ mol}}{\text{L}}\right)^2$$

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

so  $r = k [A]^1 [B]^2$  ∴  $y = 1$