Rates of reaction components

In General:

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Sample problem: The rate of formation of NH_3 in the reaction $N_2(g) + 3\ H_2 \rightarrow 2\ NH_3(g)$ was reported as 1.2 mmol $L^{-1}\ s^{-1}$ under a certain set of conditions. What is the rate of consumption of H_2?

The rate of a reaction may depend upon:

* Concentration of reactants
* Concentration of products
* Mechanism of the reaction
* Time

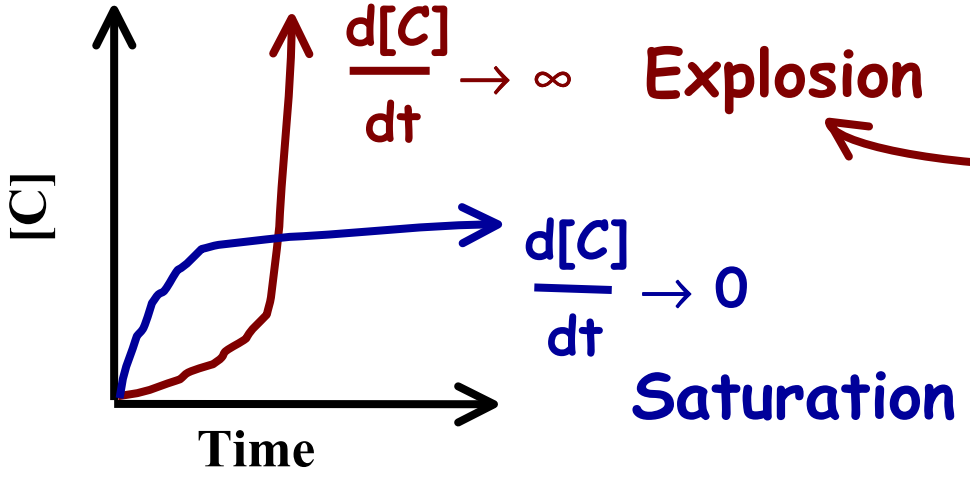
Rate laws

$A + B \rightarrow C$

$$\frac{dC}{dt} = f([A],[B],[C],t)$$

Expression relating rate to concentrations and time

Many different functional forms are in principle possible!



Reaction rate becomes catastrophically fast: heat or moles of gas produced faster than the surroundings can respond. Supersonic!

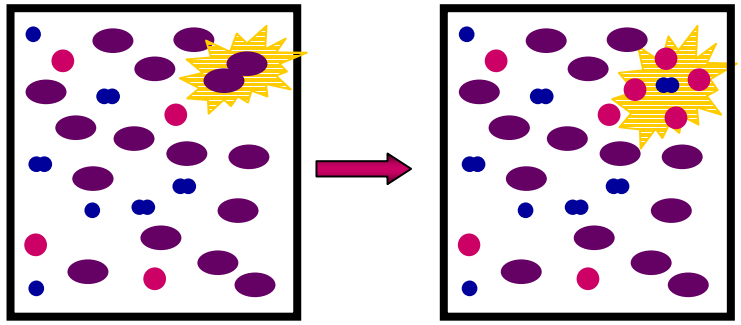
An Empirical Rate Law:
An experimentally determined, macroscopic rate law

Example: Decomposition of N_2O_5

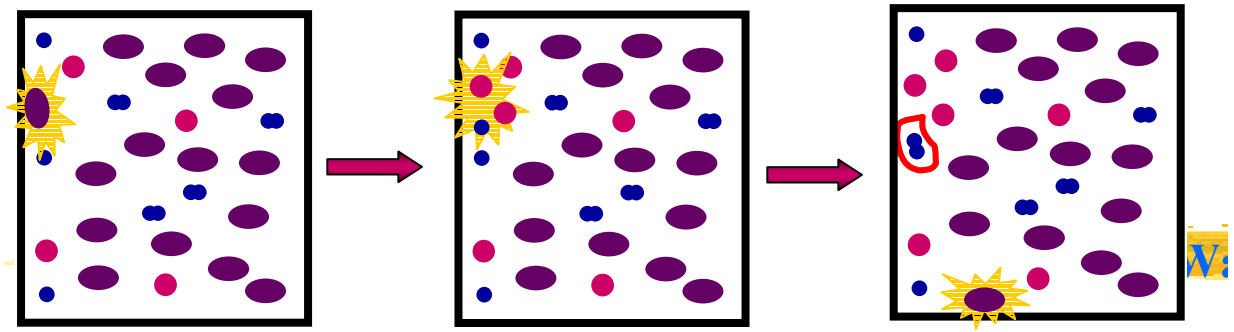
$$N_2O_5 \rightarrow 2\ NO_2 + 1/2\ O_2 \qquad \frac{d[N_2O_5]}{dt} = f([N_2O_5],[N_2O],[O_2],\ldots,t)?$$

The rate law depends on the overall microscopic mechanism and cannot in general be inferred from the net reaction!

For example, the following two mechanisms will give very different rate laws for the decomposition of N_2O_5:

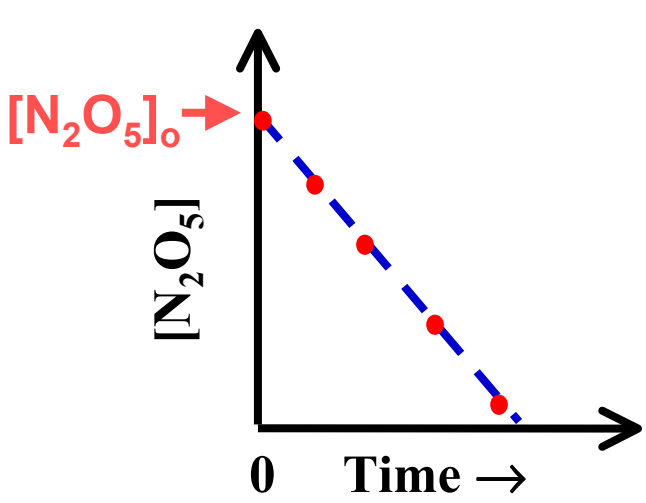


Bimolecular collision results in the formation of 4 NO_2 and one O_2

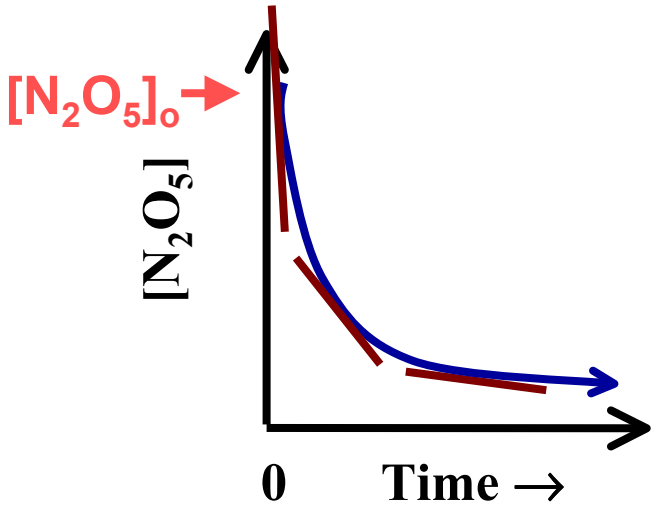


Collision with the wall results in the formation of 2 NO_2 and one O

How do we find the rate law?



OR



$[N_2O_5](t) = -kt + [N_2O_5]_o$

$[N_2O_5](t) = [N_2O_5]_o\, e^{-kt}$

$$\frac{d[N_2O_5]}{dt} = -k$$

$$\frac{d[N_2O_5]}{dt} = -k\,[N_2O_5]^1$$

Rate Constant

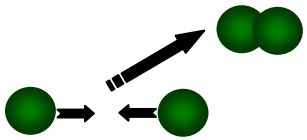
$$\Rightarrow \frac{d[N_2O_5]}{dt} = -k\,[N_2O_5]^0$$

A First Order Rate Law

A Zero Order Rate Law

Empirical rate laws

$A \rightarrow B$



If $\frac{-d[A]}{dt} = k\,[A]^0$ ..... 0^{th} Order

If $\frac{-d[A]}{dt} = k\,[A]^1$ ..... 1^{st} Order

If $\frac{-d[A]}{dt} = k\,[A]^2$ ..... 2^{nd} Order

⋮

$A + B \rightarrow C$

If $\frac{-d[A]}{dt} = k\,[A][B]$

Overall 2^{nd} Order

1^{st} order in A

1^{st} order in B

If $\frac{-d[A]}{dt} = k\,[A]^2\,[B]$

Overall 3^{rd} Order

2^{nd} order in A

1^{st} order in B

...

Sample Problem:

The reaction $2NO + Cl_2 \rightarrow 2NOCl$ was studied at -10°C. The following data were obtained for the rate of loss of Cl_2.

Measure-ment	$[NO]_o$	$[Cl_2]_o$	$\left.\frac{d[Cl_2]}{dt}\right\|_o$
1	0.10 M	0.10 M	-0.18 M/s
2	0.10 M	0.20 M	-0.35 M/s
3	0.20 M	0.20 M	-1.45 M/s

(a) What is the rate law?

(b) What is the rate constant?