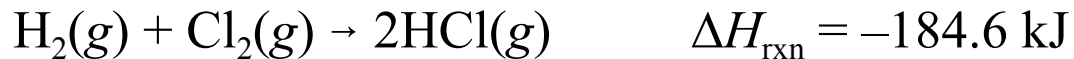


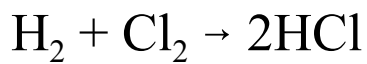
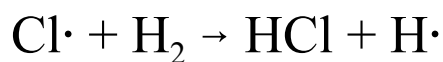
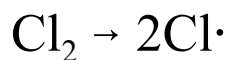
## Mechanism of a Reaction

- ☞ The mechanism of a chemical reaction is the set of microscopic steps by which atoms and molecules are converted from reactants into products.
- ☞ The macroscopic stoichiometry of a conventional balanced chemical equation *rarely* is the same as the mechanism.
- ☞ Mechanisms are deduced indirectly from experimental data on how fast reactions proceed under various conditions – the *kinetics* of the reaction.

## Example of a Simple Reaction and Its Proposed Mechanism



Proposed Mechanism:

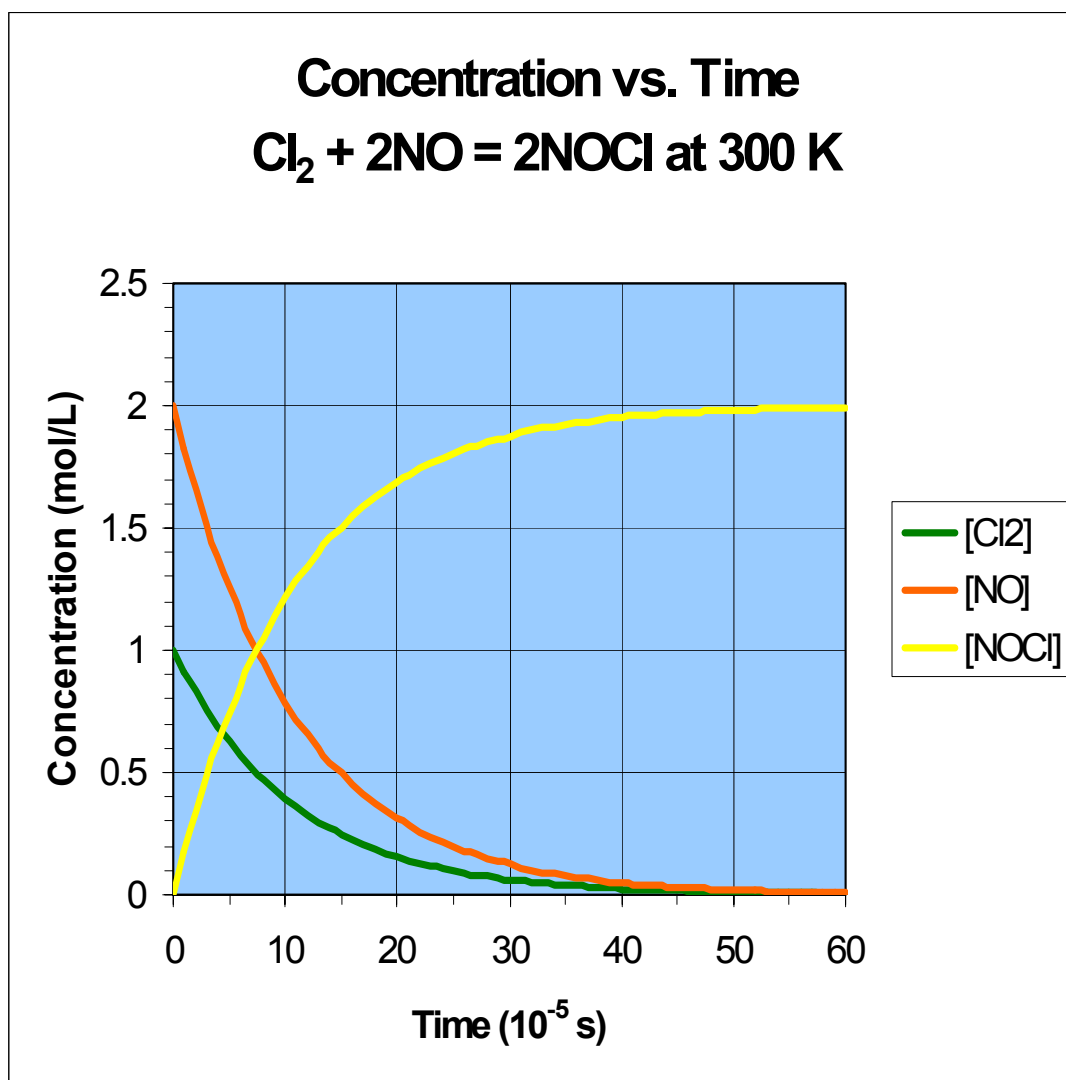


☞ Nothing about the overall stoichiometry of the reaction suggests that this is the mechanism!

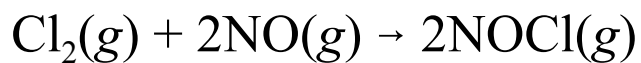
## Defining *Rate*

- ☞ *Rate* for a chemical reaction can be defined in terms of the change in concentration (or amount) of reactants or products with time.
  
- ☞ Ideally, for any point in the course of the reaction, *Rate* should be defined so as to give the same number regardless of the species (reactant or product) on which it is based.
  - *Rate* should be defined on the basis of the stoichiometry of the reaction.
  
  - *Rate* is defined to be a positive number.

## Concentration Changes with Time



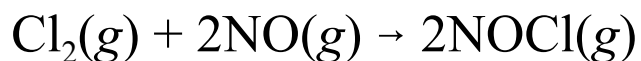
## Rate Based on Loss of $[\text{Cl}_2]$



$$\text{Rate} = \frac{-\Delta[\text{Cl}_2]}{\Delta t} = \frac{-([\text{Cl}_2]_2 - [\text{Cl}_2]_1)}{t_2 - t_1}$$

- $[\text{Cl}_2]_2 - [\text{Cl}_2]_1$  is negative, because  $\text{Cl}_2$  is being consumed.
- Negative sign in  $-\Delta[\text{Cl}_2]/\Delta t$  makes *Rate* a positive number.

## Rate Based on Loss of [NO]

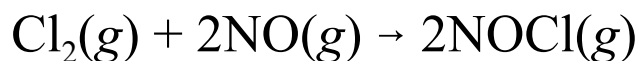


$$\frac{-\Delta[\text{NO}]}{\Delta t} = \frac{-([\text{NO}]_2 - [\text{NO}]_1)}{t_2 - t_1}$$

- $-\Delta[\text{NO}]/\Delta t = 2 \times \{-\Delta[\text{Cl}_2]/\Delta t\}$ , because 2 mol NO are consumed for every 1 mol  $\text{Cl}_2$  consumed.
- To avoid ambiguity, we define rate on the basis of [NO] as

$$\text{Rate} = \frac{-1/2\Delta[\text{NO}]}{\Delta t} = \frac{-1/2([\text{NO}]_2 - [\text{NO}]_1)}{t_2 - t_1}$$

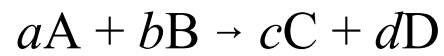
## Rate Based on Gain of [NOCl]



$$\text{Rate} = \frac{+1/2\Delta[\text{NOCl}]}{\Delta t} = \frac{+1/2([\text{NOCl}]_2 - [\text{NOCl}]_1)}{t_2 - t_1}$$

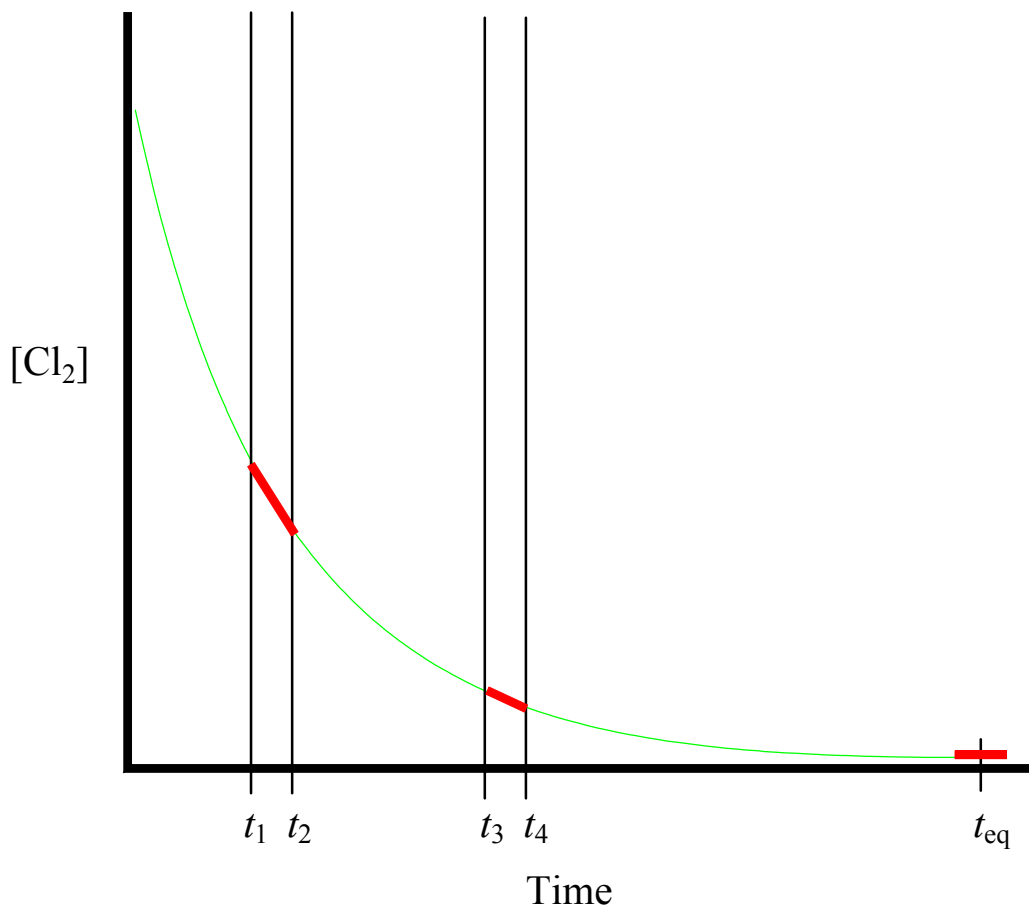
- $\Delta[\text{NOCl}]/\Delta t$  is positive, so *Rate* will be positive without the need to add a negative sign.
- $\Delta[\text{NOCl}]/\Delta t = 2 \times \{-\Delta[\text{Cl}_2]/\Delta t\}$ , because 2 mol NOCl are produced for every 1 mol  $\text{Cl}_2$  consumed.

## Defining *Rate* for a General Reaction



$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

## *Rate and Slope*



- If the interval between  $t_1$  and  $t_2$  is small, the curve is approximately a straight line, whose slope is the negative of the *Rate*:

$$\text{Rate} = \frac{-\Delta[\text{Cl}_2]}{\Delta t} = -\text{slope}$$

## Instantaneous Rate

- The approximation that the curve is nearly a straight line becomes better as  $\Delta t$  becomes smaller.
- At the limit where  $\Delta t$  becomes infinitesimally small, the segment of the curve *is* a straight line, the negative of whose slope gives the *instantaneous rate* at a point in time.
- To indicate instantaneous rate, we use the notation  $d$  instead of  $\Delta$ :

$$\text{Rate} = \frac{-d[\text{Cl}_2]}{dt} = -\text{slope}$$

## Changing *Rate* and Equilibrium

- The magnitude of slope, and therefore *Rate*, declines over time.
  - ☞ Reaction rate slows down as the reaction proceeds.
- At  $t_{\text{eq}}$ , when slope = 0, *Rate* = 0, and the reaction has reached *equilibrium*.
  - ☞ *Rate* = 0 does not mean the reaction has stopped, just that it has reached equilibrium.

## **Initial Rate**

- ☞ Because rate changes over time, comparisons between reaction rates need to be made at the same elapsed time.
- ☞ For convenience, comparisons are often made between *initial rates*, taken at the very beginning of the reaction ( $t = 0$ ).

## Differential Rate Law

- ☞ The differential rate law is a mathematical equation that shows the *dependence of rate on concentration*.

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n \dots$$

where  $m = \text{order}$  with respect to [A]  
 $n = \text{order}$  with respect to [B]  
 $m + n + \dots = \text{overall order} = \omega$   
 $k = \text{rate constant}$  for the reaction at a certain temperature

- ☞ ***The explicit form of the differential rate law for a particular reaction must be experimentally determined and cannot in general be deduced from the overall stoichiometry of the reaction.***

- ☞ If  $\omega$  is the overall order of the rate law, the units of  $k$  will be

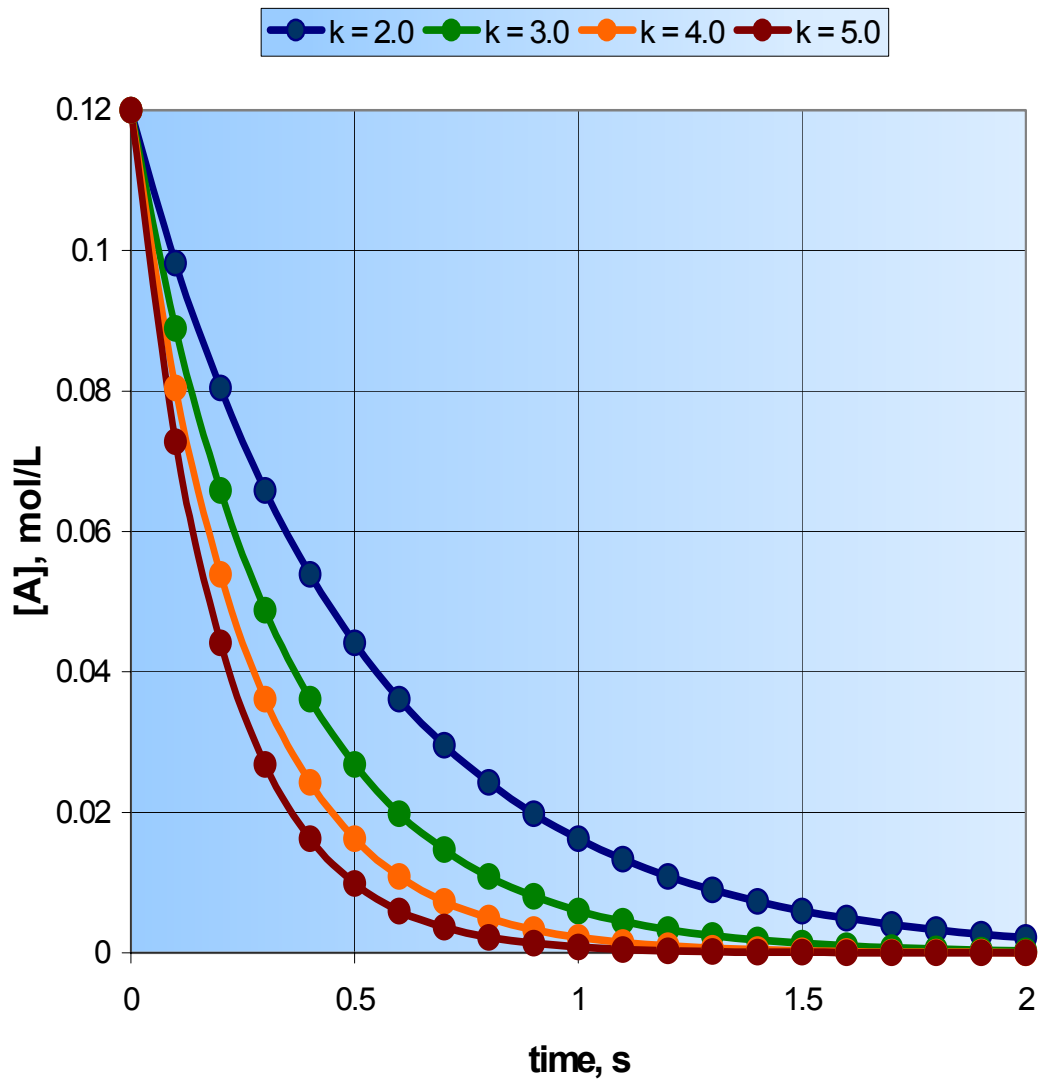
$$k = (\text{conc. units})^{-(\omega - 1)} (\text{time})^{-1}$$

- ☞ The larger the value of  $k$ , the higher the rate will be for any particular set of concentrations.

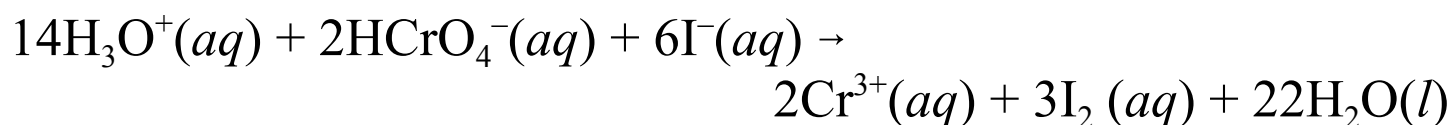
# Hypothetical First-Order Reaction, $A \rightarrow B$

$$\text{Rate} = k[A]$$

Effect of  $k$  Value on Rate of a First-Order Reaction



## Some Reactions and Their Experimental Rate Laws



$$\text{Rate} = k[\text{HCrO}_4^-][\text{I}^-][\text{H}_3\text{O}^+]$$

☞ **Note:** Orders do not reliably match stoichiometric coefficients.

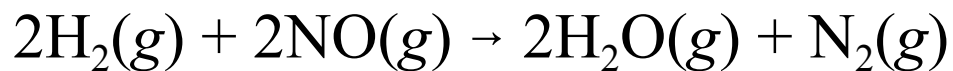
Example: Determine the rate law and value of  $k$  for the following reaction at 300K.



$[\text{N}_2\text{O}_5]$ (mol/L)	Initial Rate (mol/L/sec)
0.25	$1.0 \times 10^{-5}$
0.50	$2.0 \times 10^{-5}$

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

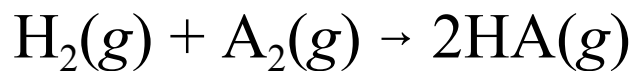
Example: Determine the rate law and value of  $k$  for the following reaction at  $800^\circ\text{C}$ .



$p_{\text{H}_2}$ (atm)	$p_{\text{NO}}$ (atm)	Initial Rate (atm/min)
0.13	0.39	0.050
0.26	0.39	0.10
0.13	0.78	0.20
0.26	0.78	0.40

$$\text{Rate} = k p_{\text{H}_2} p_{\text{NO}}^2$$

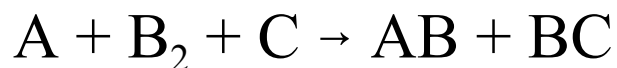
Example: Determine the rate law for the following hypothetical reaction:



$[\text{H}_2]$ (mol/L)	$[\text{A}_2]$ (mol/L)	Initial Rate (mol/L/sec)
0.30	0.30	0.020
0.30	1.20	0.040
1.20	0.30	0.080

$$\text{Rate} = k[\text{H}_2][\text{A}_2]^{1/2}$$

Example: Determine the differential rate law expression and value of  $k$  for the reaction

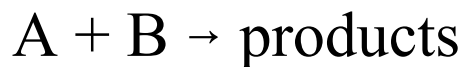


given the following kinetic data:

Exp.	[A], M	[B <sub>2</sub> ], M	[C], M	Rate, M·s <sup>-1</sup>
#1	0.128	0.111	0.702	1.07 x 10 <sup>-3</sup>
#2	0.384	0.111	0.702	3.21 x 10 <sup>-3</sup>
#3	0.128	0.444	0.702	2.14 x 10 <sup>-3</sup>
#4	0.128	0.444	0.351	2.14 x 10 <sup>-3</sup>

$$Rate = k[A][B_2]^{1/2}$$

Example: Consider the following hypothetical reaction and rate data:



[A] (mol/L)	[B] (mol/L)	Initial rate (mol/L/min)
$5.30 \times 10^{-2}$	$7.20 \times 10^{-2}$	$3.70 \times 10^{-3}$
$6.42 \times 10^{-2}$	$7.20 \times 10^{-2}$	$4.07 \times 10^{-3}$
$6.42 \times 10^{-2}$	$9.32 \times 10^{-2}$	$5.99 \times 10^{-3}$

$$\text{Rate} = k[A]^{1/2}[B]^{3/2}$$