Mechanism of a Reaction
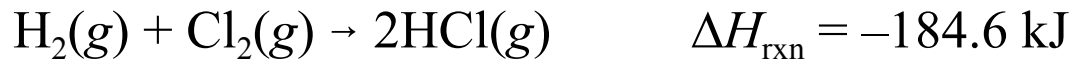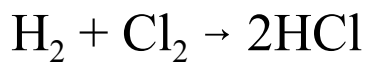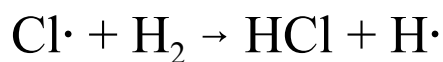
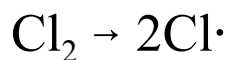☞ The mechanism of a chemical reaction is the set of microscopic steps by which atoms and molecules are converted from reactants into products.

☞ 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

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad \Delta H_{rxn} = -184.6 \text{ kJ}$$

Proposed Mechanism:

$$Cl_2 \rightarrow 2Cl\cdot$$

$$Cl\cdot + H_2 \rightarrow HCl + H\cdot$$

$$H\cdot + Cl\cdot \rightarrow HCl$$

$$\overline{}$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

☞ 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.
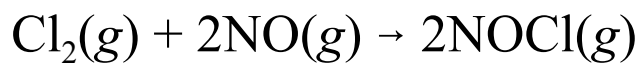
☞ Ideally, for any point in the course of the reaction, *Rate* should be defined so as to give the same number regardless of the species (reactant or product) on which it is based.

- *Rate* should be defined on the basis of the stoichiometry of the reaction.

- *Rate* is defined to be a positive number.
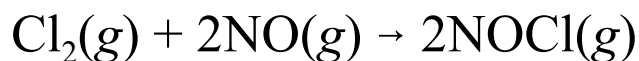
Concentration Changes with Time

Concentration vs. Time
$Cl_2 + 2NO = 2NOCl$ at 300 K

Concentration (mol/L) vs. Time (10^{-5} s)

[Cl2]
[NO]
[NOCl]
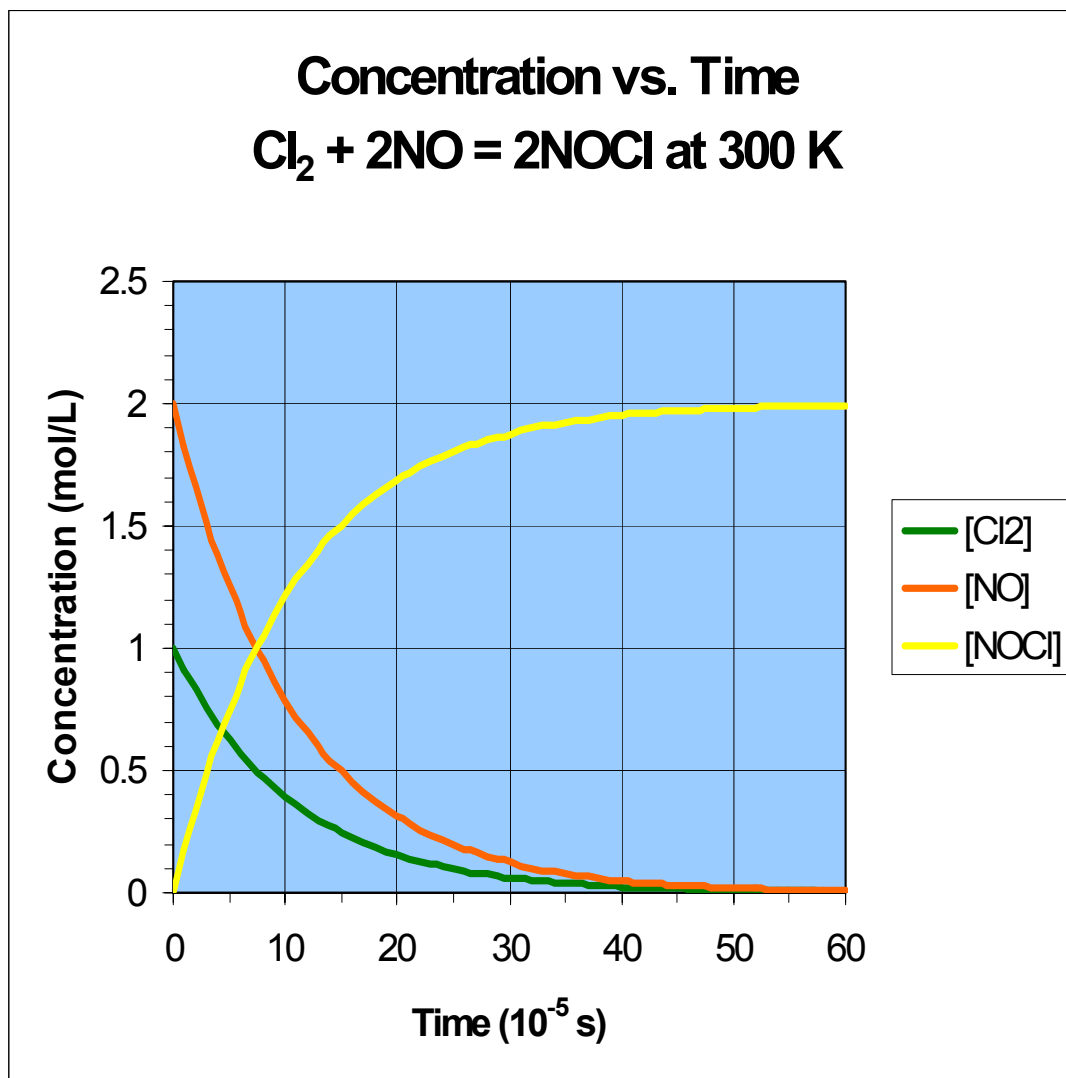
Rate Based on Loss of $[Cl_2]$

$$Cl_2(g) + 2NO(g) \rightarrow 2NOCl(g)$$

$$Rate = \frac{-\Delta[Cl_2]}{\Delta t} = \frac{-([Cl_2]_2 - [Cl_2]_1)}{t_2 - t_1}$$

- $[Cl_2]_2 - [[Cl_2]_1$ is negative, because Cl_2 is being consumed.

- Negative sign in $-\Delta[Cl_2]/\Delta t$ makes *Rate* a positive number.
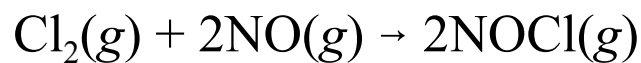
Rate Based on Loss of [NO]

$$Cl_2(g) + 2NO(g) \rightarrow 2NOCl(g)$$

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

- $-\Delta[NO]/\Delta t = 2 \times \{-\Delta[Cl_2]/\Delta t\}$, because 2 mol NO are consumed for every 1 mol Cl_2 consumed.

- To avoid ambiguity, we define rate on the basis of [NO] as

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

Rate Based on Gain of [NOCl]

$$Cl_2(g) + 2NO(g) \rightarrow 2NOCl(g)$$

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

- $\Delta[NOCl]/\Delta t$ is positive, so *Rate* will be positive without the need to add a negative sign.

- $\Delta[NOCl]/\Delta t = 2 \times \{-\Delta[Cl_2]/\Delta t\}$, because 2 mol NOCl are produced for every 1 mol Cl_2 consumed.

Defining *Rate* for a General Reaction

$$aA + bB \rightarrow cC + dD$$
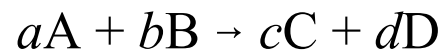
$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

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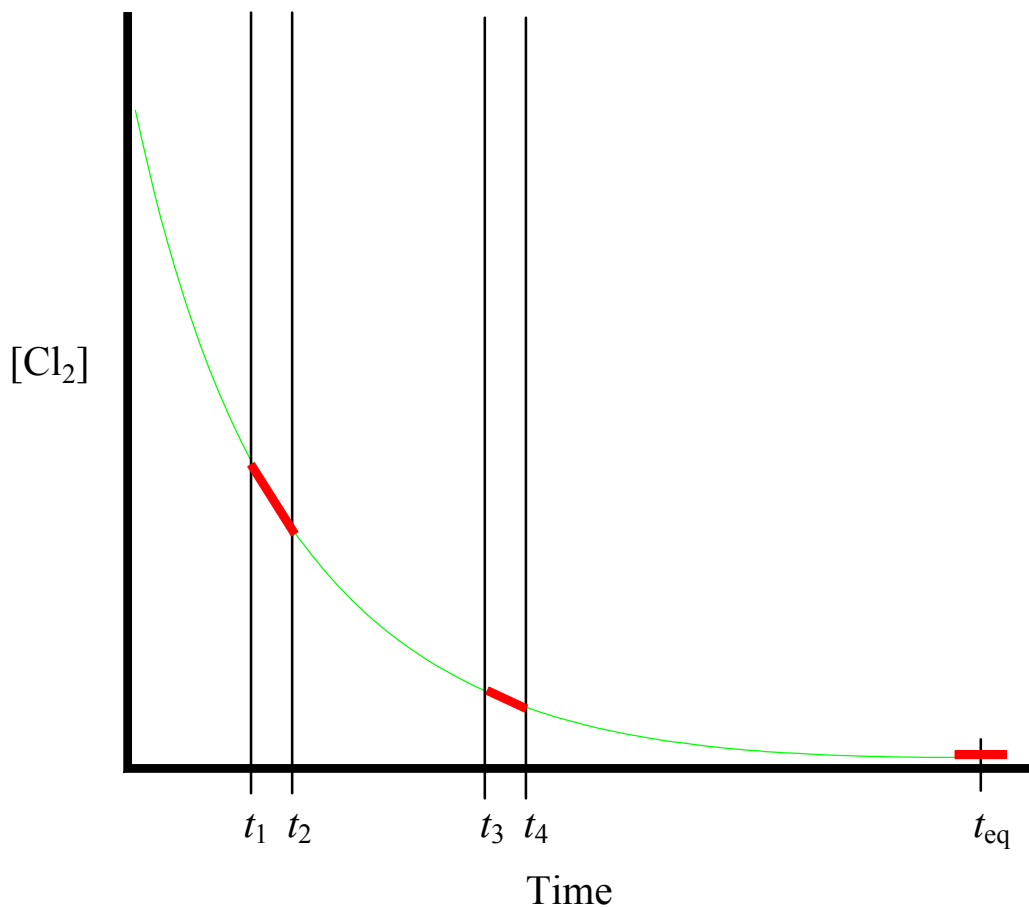
- If the interval between t_1 and t_2 is small, the curve is approximately a straight line, whose slope is the negative of the *Rate*:

$$Rate = \frac{-\Delta[Cl_2]}{\Delta t} = -slope$$

Instantaneous Rate

- The approximation that the curve is nearly a straight line becomes better as Δt becomes smaller.

- At the limit where Δt 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 Δ:

$$Rate = \frac{-d[Cl_2]}{dt} = -\text{slope}$$

Changing *Rate* and Equilibrium

- The magnitude of slope, and therefore *Rate*, declines over time.

    ☞ Reaction rate slows down as the reaction proceeds.

- At t_{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.*

$$Rate = k[A]^m[B]^n \ldots$$

where $m = $ **order** with respect to [A]
$n = $ order with respect to [B]
$m + n + \ldots = $ **overall order** $= \omega$
$k = $ *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.***

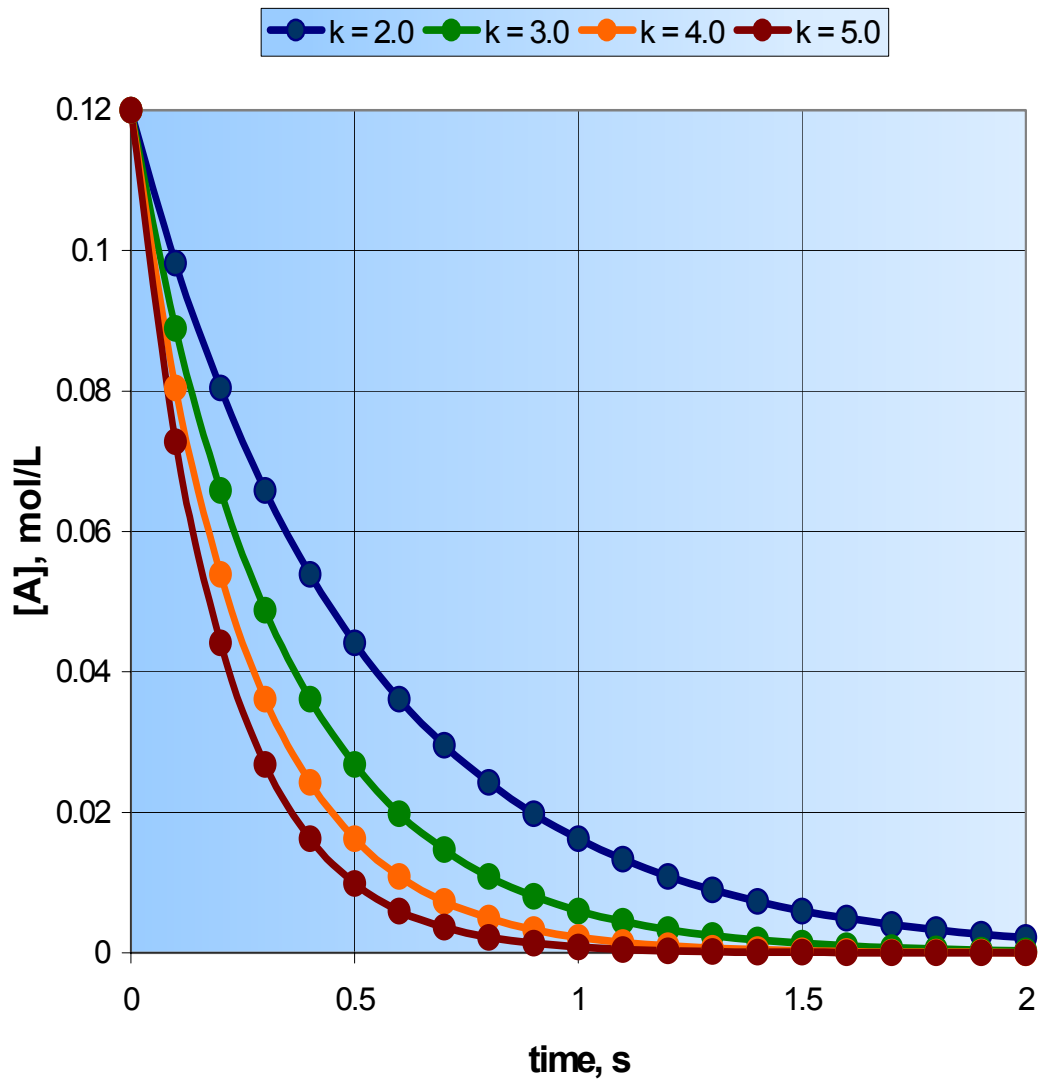☞ If ω is the overall order of the rate law, the units of k will be

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

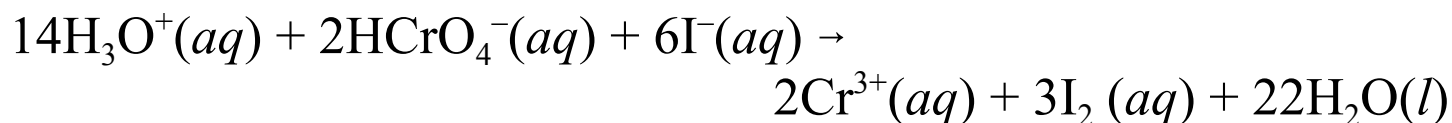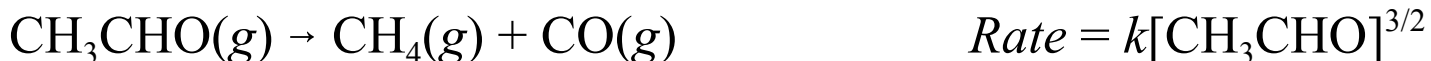☞ The larger the value of k, the higher the rate will be for any particular set of concentrations.

Hypothetical First-Order Reaction, A → B
$Rate = k[A]$

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

Legend: k = 2.0, k = 3.0, k = 4.0, k = 5.0

[A], mol/L

time, s

Some Reactions and Their Experimental Rate Laws

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ $Rate = k[N_2O_5]$

$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$ $Rate = k[NO_2][F_2]$

$NO(g) + N_2O_5(g) \rightarrow 3NO_2(g)$ $Rate = k[N_2O_5]$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $Rate = k[NO]^2[O_2]$

$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ $Rate = k[CH_3CHO]^{3/2}$

$14H_3O^+(aq) + 2HCrO_4^-(aq) + 6I^-(aq) \rightarrow$
$$2Cr^{3+}(aq) + 3I_2\ (aq) + 22H_2O(l)$$

$$Rate = k[HCrO_4^-][I^-][H_3O^+]$$

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

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

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

$[N_2O_5]$ (mol/L)	Initial Rate (mol/L/sec)
0.25	1.0×10^{-5}
0.50	2.0×10^{-5}

$$Rate = k[N_2O_5]$$

Example: Determine the rate law and value of k for the following reaction at 800°C.

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$
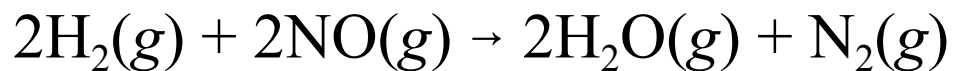
p_{H_2} (atm)	p_{NO} (atm)	Initial Rate (atm/min)
0.13	0.39	0.050
0.26	0.39	0.10
0.13	0.78	0.20
0.26	0.78	0.40

$$Rate = k p_{H_2} p_{NO}^2$$

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

$$H_2(g) + A_2(g) \rightarrow 2HA(g)$$
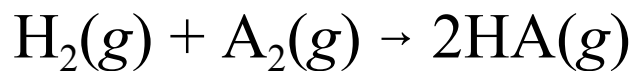
[H$_2$] (mol/L)	[A$_2$] (mol/L)	Initial Rate (mol/L/sec)
0.30	0.30	0.020
0.30	1.20	0.040
1.20	0.30	0.080

$$Rate = k[H_2][A_2]^{1/2}$$

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

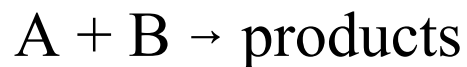$$A + B_2 + C \rightarrow AB + BC$$
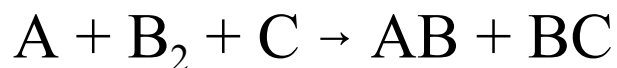
given the following kinetic data:

Exp.	[A], M	[B$_2$], M	[C], M	Rate, M·s^{-1}
#1	0.128	0.111	0.702	1.07 x 10^{-3}
#2	0.384	0.111	0.702	3.21 x 10^{-3}
#3	0.128	0.444	0.702	2.14 x 10^{-3}
#4	0.128	0.444	0.351	2.14 x 10^{-3}

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

Example: Consider the following hypothetical reaction and rate data:

$$A + B \rightarrow products$$

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

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