Chemical Kinetics

What factors determines the speed of a chemical reaction?

Concentration of reactants

Physical state of reactants

Temperature

Catalysts

Reaction Rate

Change in concentration of reactants or products in time

Usually concentration is in molarity (moles/liter)

Reaction rate expressed as

moles/liter sec or M/sec

Consider the reaction of butyl chloride with water to form butyl alcohol and hydrochloric acid

$$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCL($$

Reaction Rates and Concentration

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

TABLE 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

Data suggest that

$$Rate = k[NH_4^+][NO_2^-]$$

$$k = rate\ constant$$

k changes with temperature

Using Initial Rates to Determine Rate Laws

Observe the effect of changing the initial concentrations on the initial rate

$$A + B \rightarrow C$$

Experiment	[A](M)	[B](M)	Initial Rate (M/sec)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

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

Experiments 1 & 2 require $n=0$

Experiments 1 & 3 require $m=2$

$$Rate = k[A]^2$$

Change of Concentration with Time

First order reaction has the rate law

$$Rate = -\frac{\Delta[A]}{\Delta t} = k[A]$$

or

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

Integrating this results in

$$ln\frac{[A(t)]}{[A(0)]} = -kt$$

or

$$[A(t)] = [A(0)]exp(-kt)$$

Second Order Reaction

Rate depends on the reactant concentration squared

$$Rate = -\frac{d[A]}{dt} = k[A]^2$$

$$\frac{d[A]}{[A]^2} = -kdt$$

$$\int_{[A(0)]}^{[A(t)]} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\frac{1}{[A(t)]} = kt + \frac{1}{[A(0)]}$$

Reaction Mechanisms

Order in which bonds are broken & forme

Processes that occur in a
single event or step
are called
elementary processes (steps)

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

molecularity = 2

$$CH_3NC(g) \rightarrow CH_3CN(g)$$

molecularity = 1

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$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

molecularity = 2 or bimolecular

$$CH_3NC(g) \rightarrow CH_3CN(g)$$

molecularity = 1 or unimolecular

???????????????

molecularity =3 or termolecular

Multistep Reactions

Occur via a sequence of elementary reactions

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Occurs in two bimolecular elementary steps

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

$NO_3(g)$ *is a reactive intermediate*

Rate Laws for Elementary Steps

If we know that a reaction is an elementary step then we know its rate law

TABLE 14.3 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

Rate Laws for Multistep Reactions

Most chemical reactions occur via a series of elementary steps

Each step has its own rate constant k

The overall rate of the reaction is determined by the slowest step

This is called the rate determining step

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

$$Rate = k[NO_2]^2$$

$$step\ 1\ : NO_2 + NO_2 \rightarrow NO_3 + NO\ ;\ k_1$$

$$step\ 2\ : NO_3 + CO \rightarrow NO_2 + CO_2\ ;\ k_2$$

If $k_2 >> k_1$ step 1 is rate determining

Mechanisims with an Initial Fast Step

The reaction

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

Experimentally determined rate law

$$Rate = k[NO]^2[Br_2]$$

Suggests that the
elementary reaction is termolecular

This is unlikely

Try to construct a mechanism involving
unimolecular and/or bimolecular steps

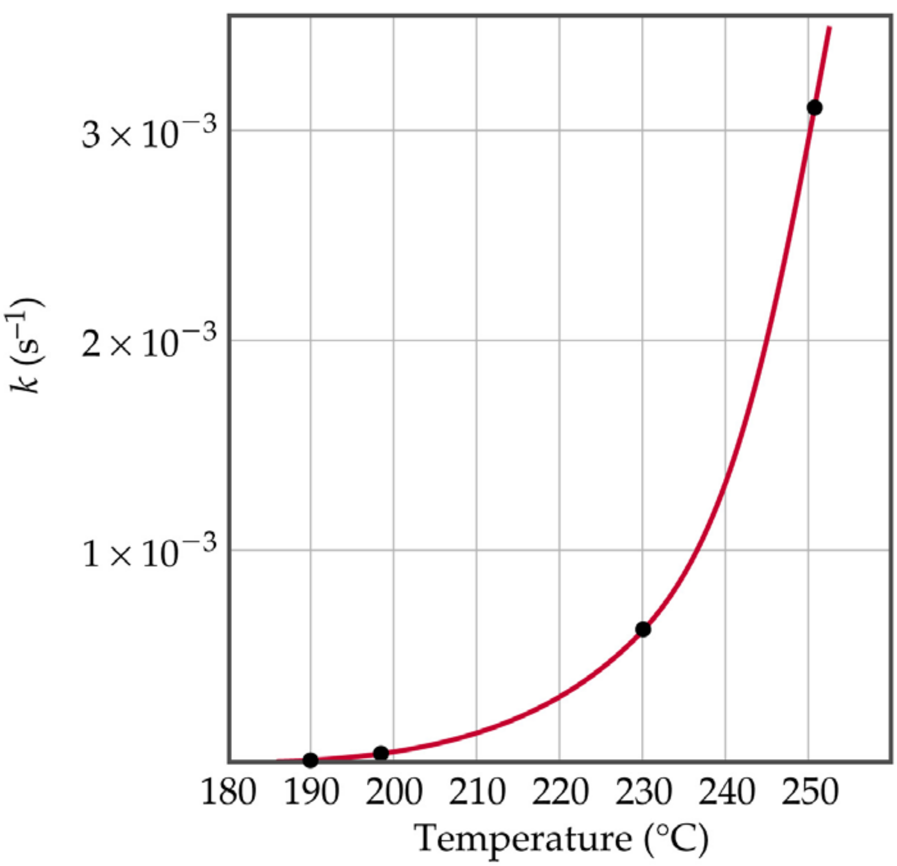
Temperature & Rate

The rate of most chemical reactions

increases with increasing temperature

Rate increase is a result of *k* increasing

$$H_3C - NC \xrightarrow{k} H_3C - CN$$



The Arrhenius Equation

$$k = A\,exp(-E_a / RT)$$

A is the frequency factor

E_a is the activation energy

$$H_3C-NC \xrightarrow{k} H_3C-CN$$

T(^{0}C)	k(s^{-1})
189.7	2.52 x 10^{-5}
198.9	5.25 x 10^{-5}
230.3	6.30 x 10^{-4}
251.2	3.16 x 10^{-3}

Calculate :

Activation Energy
Rate constant ant 430.0 K

Catalysis

The process in which one uses a substance to accelerate the rate of a chemical reaction without having the substance undergo a permanent chemical change in the process

A catalyst is the substance that accelerates the chemical reaction and is unchanged afterwards

Two types of catalysts

Homogeneous

Heterogeneous

Heterogeneous Catalysis

The catalyst exists in a different phase from the reactant molecules

Catalyst is usually a solid

Reactants may be gases or liquids

Initial step in heterogeneous catalysis is adsorption of reactants onto the surface of the catalyst

Places where reactants are adsorbed are called reactive sites

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \qquad \Delta H^0 = -137 kJ/mol$$