Chapter. 7 Abiotic and Biotic Transformations

◎ Abiotic transformation

a) hydrolysis
- addition of water to a molecule (usu. to functional groups)
- often enhanced by the presence of acids or bases

b) redox reaction
- promoted by low conc. of oxygen radicals, mineral surfaces, UV/ozone/Fenton's reagent/TiO_2 (collectively called AOP)/Fe^0...

c) photolysis
- light-induced redox reaction
- chemicals must be on surface or where light can reach

◎ Biotic transformation

a) biodegradation vs. mineralization

b) the most significant removal pathway of contaminants from in natural env.

1. The Governing Variables: Chemical structure, Presence of reactive species, and Availability (p. 335)

- amenable chemical structure
- appropriate reactive species or microorganisms
- physical availability (not sorbed or in NAPL phase)

1.1. Chemical structure: The basis for reactivity in abiotic and biotic transformations

1) structure-biodegradability

a) recalcitrant chemicals:
- branched hydrocarbons
- saturated hydrocarbons
- increased halogenation
- high hydrophobicity

b) amenable chemicals; structures similar to normal metabolic intermediates

2) abiotic degradation

a) hydrolysis;
- electron rich species (like water) attacks an e-poor area (carbon) of an organic molecule (nucleophilic rxn)
- e-poor area generated by difference in "electronegativity"

b) oxidation state of contaminants (esp. carbon);
- (rule) when bonded to organic C, the oxidation state of H is +1, of O is -2, and of halogens is -1, respectively
  (e.g.) CH_4 and CCl_4 (i.e., the most reduced C vs. the most oxidized C)
- general rules for the determination of oxidation state (Table 7.1)

- C in PCE, CCl_4; highly oxidized --> degraded by reacting with reductants
C in aromatics (e.g. benzene..); reduced --> degraded by oxidation rxn.

3) electrophilic substitution of aromatic compounds (also in aliphatics)
   a) electron-withdrawing groups increase the C oxidation state (e.g., -Cl, $-NO_2$)
      : substitution of a aromatic ring with deactivating groups (Table 7.2)
      --> make the ring more electropositive
      --> lower the chance of nucleophilic attack
   b) electron-donating groups increase the C reduction state (e.g., $-NH_2$, -OH)
      : substitution of a aromatic ring with activating groups (Table 7.2)
      --> make the ring more reactive to electrophilic attack

1.2. Presence of transforming species

a) electron-withdrawing groups
b) oxidants/reductants
   - reduced contaminants are to be degraded through oxidation
     e.g.) phenol by hydroxyl radicals (-OH•)
   - oxidized contaminants are to be degraded through reduction
     e.g.) CCl_4 by pyrite (FeS)
c) appropriate microorganisms; consortium vs. a bacterium

1.3. Sorption and NAPLs: Inaccessibility to transforming processes

a) sorption/desorption
   - desorption rate controls biotransformation
   - sometimes, sorbed compounds can be degraded without the necessity of desorption (degraded as they are)
   - some microbes produce biosurfactants to facilitate desorption
     e.g.) rhamnolipids by *Pesudomonas fluorescence*
b) sequestration (aging);
   - post-sorption process that contaminants move far inside the sorbents matrix where the compounds are physically protected
   - formation of desorption-resistant fractions
c) NAPLs
   - partitioning medium for organic contaminants
   - dissolution rate from NAPLs is important
   - some microbes attach on NAPL surfaces, and directly utilize contaminants in NAPL phase (but, not well known mechanism)

1.4. Other variables affecting transformation processes

a) dissolved oxygen and oxidation-reduction potential
   - aerobic vs. anaerobic rxns
     . terminal electron acceptors (e.g., O_2, NO_3^-, SO_4^{2-}, CO_2)

. O_2 is the most efficient energy source

. redox potential of the env. determines TEA to be used (assuming that all are readily available)

. anoxic conditions (generally, below 1-2 mg O_2/L)

b) temeprature

- *Van't Hoff Rule*; effect of temp. on reaction rates

$$Y = Ae^{\frac{-E_a}{RT}}$$

Y, A; Arrhenius constants

E_a; activation energy (kcal/mole)

- an empirical euqation

$$k_{T2} = k_{T1} \cdot \Theta^{T2-T1}$$

Θ; 1.01 - 1.11 (depending on the system)

e.g.) 1.088 for the metabolism of hydrocarbon-degrading bacteria

k_{T1}; reaction rate at temperature 1

k_{T2}; reaction rate at temperature 2

- Q_{10} value; reaction rate 2-fold increase with 10°C increase

c) pH

- biological system; sensitive to pH

. pH 6 to 9 for most bacteria

. pH 4 to 6 for fungi

- abiotic system; may or may not sensitive to pH

. Fenton's reaction; effective at pH 2-4 (see p. 615-620)

d) moisture content

e) ionic strength

f) toxicity of contaminants (-> inhibition of degrading microorganisms)

g) quenching of free radicals

e.g.) OH radicals quenched by bicarbonate, chloride,...

2. Rates of Transformation (p. 342)

1) Reaction kinetics

a) transformation kinetics; zero-, first-, second-order reactions

$$\frac{-d[C]}{dt} = k[C]^n$$

[C]; contaminant concentration (mg/L)

k; proportionality contant (units dependent on rxn order)

n; reaction order (i.e, 0, 1, 2)

b) zero-order reaction

- when n = 0, $\frac{-d[C]}{dt} = k$

- integrated form; $C_t = C_0 - kt$

- contaminant concentration decreases **to a fixed amount** with time
- independent of contaminant concentration
- linear transformation rate (i.e., $t_{1/2}$ = 1/2[C_0])

c) first-order reaction

- when n = 1, $\frac{-d[C]}{dt}$ = k[C]
- integrated form; $C_t = C_0 \cdot e^{-kt}$
- contaminant concentration decreases **to a fixed rate (k)** with time
- k; first-order rate constant (unit; day^{-1})
- k is independent of contaminant concentration
- $t_{1/2}$ = 0.693/k (independent of [C_0])

d) second order reaction

- rate of change is proportional to two species
- when n = 2, $\frac{-d[C_1]}{dt}$ = k[C_1][C_2]

  C_1; contaminant

  C_2; another reactant
- contaminants and another reactant

  -d[C]/dt = k[C][enzyme] for biological transformations

  -d[C]/dt - k[C][OH radical] for radical-mediated degradations
- often, [C_2] is at steady state, meaning concentration constant over time (e.g., provided enough consistently)

  -d[enz]/dt ≒ 0 (= 0)

  -d[OH•]/dt ≒ 0 (= 0)

  -> only [C_1] then affects the rate of rxn.

  -> -d[C_1]/dt = k'[C_1] (k'= k[enz] or k[OH])

  -> "***pseudo-first order kinetics***" ($t_{1/2}$ = 0.693/k')

  ; applicable most biotic and abiotic environmental reactions
- Example 7.2

2) Saturation kinetics

a) used to describe reaction rates catalyzed by a fixed mass of catalyst (e.g.) enzymatic reaction, inorganic surface catalysis

b) reaction rates increase linearly as a function of substance concentration, but then the rate of change decreases to a maximum level (V_{max})

c) Michaelis-Menton kinetics (Fig. 7.1)

$$V = V_{max} \cdot \frac{C}{C + K_m}$$

V; rate of transformation (mg/L-h)

V_{max}; maximum rate of transformation (mg/L-h)

C; contaminant concentration (mg/L)

K_m; half-saturation constant (mg/L)

- K_m
  . the contaminant concentration at $1/2V_{max}$
  . shows the affinity between reactants (i.e., contaminant and enzyme)
- most commonly used to determine "initial reaction rates"
- competitive and noncompetitive inhibition

3. Abiotic Transformation (p. 346)

- not as important as biotic transformation in the environment (as a pollutants' removal mechanism)
- substitution, hydrolysis, elimination, oxidation-reduction,...

3.1. Nucleophilic substitution and hydrolysis

a) substitution reaction occurs at electron-poor area of a compound

b) nucleophilic attack can be promoted by OH^-, S^{2-}, Cl^-, NO_3^-...but mainly by **water**

- nucleophilic attack by water -> hydrolysis
- alkyl halides, esters, and ester-like compounds, amides are susceptible
- examples in p. 347

c) some hydrolysis rxns are acid- (H^+) or base-(OH^-) catalyzed

- pH dependence of hydrolysis (Fig. 7.2)
- rate = uncatalyzed hydrolysis (1st order)
  + acid and base-catalyzed (2nd order)

$$-dC/dt = k[C] + k_{H+}[C][H^+] + k_{OH-}[C][OH^-]$$

[C]; contaminant conc (M)

k; 1st order hydrolysis rate constant (sec^{-1})

k_{H+} = 2nd order rate constant for acid-catalyzed hydrolysis ($M^{-1}sec^{-1}$)

k_{OH-} = 2nd order rate constant for base-catalyzed hydrolysis ($M^{-1}sec^{-1}$)

- overall rate constant $k_T = k + k_{H+} + k_{OH-}$
- half-life of a compound by hydrolysis can be calculated *at a particular pH*
- hydrolysis rate data (Table 7.3) and calculation (Example 7.4)

3.2. Elimination reactions

a) removal of halogens from alkanes, alkenes,...

b) β-elimination (or dehydrohalogenation)

3.3. Oxidation

a) electron transfer reaction

b) biotic redox reaction is more important than abiotic redox reaction

c) half-reactions and standard redox potentials (Table 7.4)

d) balancing redox reactions (Example 7.5)

e) oxidation state of C of a contaminant dictates whether the compound is to be degraded through oxidation or reduction (Fig. 7.3)

f) thermodynamics (i.e, potential) vs. kinetics (i.e., observation)

g) major oxidants

- molecular oxygen; the most abundant oxidant in the env.
- mineral oxides (surface catalysis); Fe(III), Mn(III/IV) oxides
- hydroxyl radicals (-OH•)
  . transient, highly oxidizing species
  . nonspecific reaction

h) hydroxyl radicals

- generation of radicals

  (e.g.) O_2 --(e^-)--> $O_2^{\bullet -}$ --(superoxide dismutase)--> H_2O_2

  $H_2O_2 + Fe^{2+}$ --> $OH\bullet + OH^- + Fe^{3+}$

- Advanced Oxidation Porcesses (AOPs)

  (e.g.) UV/O_3, O_3/H_2O_2, Fenton's reagent,...

- hydroxyl radical rxns involve (p. 359)
  . eletrophilic addition of alkenes and aromatics
  . hydrogen abstraction
- second-order reaction

$$-\frac{d[C]}{dt} = k_{OH\bullet}[C][OH\bullet]$$

[C]; contaminant concentration (M)

[OH•]; hydroxyl radical concentration (M)

$k_{OH\bullet}$; second-order rate constant ($M^{-1}sec^{-1}$)

i) reactivity of hydroxyl radicals with contaminants (Table 7.6)

- $k_{OH\bullet}$ values provide a good indicator of the reactivity of hydroxyl radicals with organic contaminants
- $k_{OH\bullet}$ does not exceed $10^{10}M^{-1}sec^{-1}$ (i.e., the rate of diffusion of hydroxyl radicals in water)
- $k_{OH\bullet}$ above $10^9M^{-1}sec^{-1}$; reactive (to oxidize contaminants)
- $k_{OH\bullet}$ below $10^8M^{-1}sec^{-1}$; insignificantly reactive
  . competes with quenching reactions;

  $OH\bullet + O2\bullet^- + H^+$ --> $O_2 + H_2O$

  . rxn rates for quenching; 10^6 - $10^8M^{-1}sec^{-1}$

  $k_{OH\bullet}$ of bicarbonate = $1.5 \times 10^7M^{-1}sec^{-1}$

  $k_{OH\bullet}$ of carbonate = $4.2 \times 10^8M^{-1}sec^{-1}$
- highly reactive chemicals; (chlorinated)alkenes, aromatics, pesticides,...
- less reactive chemicals; chlorinated alkanes (CCl_4, $CHCl_3$, CH2Cl_2...)
- rate of contaminant oxidation by hydroxyl radicals (Example 7.6)

3.4. Reduction

a) oxidized chemicals are reduced if electrons are available

b) second-order rate constants (Table 7.7)

c) abiotic reduction; surface catalysis (Fig. 7.4)

d) reductants (reducing agents); FeS (pyrite), $FeCO_3$, H_2S

e) under the reducing natural environments, abiotic reduction rates are usually enhanced by mediators (i.e., Fe(II)-porphyrins, natural organic matter, hydroquinone/quinone)

- (oxidized) contaminants reduced as (reduced) mediators oxidized
- the oxidized mediator reduced by bulk reductants (i.e., Fe(II). sulfides)

f) zero-valent iron (i.e., iron metal; Fe^0)

- a natural reductant that readily losses electrons through corrosion

  $Fe^0 \rightleftharpoons Fe^{2+} + 2e^-$

- reductive dehalogenation in the presence of water (a proton donor)

  $\mathbf{Fe^0} + CCl_4 + H^+ \rightarrow Fe^{2+} + CCl_3H + Cl^-$

- Fe^{2+} can also serve as a reductant

  $\mathbf{Fe^{2+}} + CCl_4 + H^+ \rightarrow 2Fe^{3+} + CCl_3H + Cl^-$

- used as a medium for permeable reactive barrier (PRB) to treat halogenated alkenes such as PCE, TCE

g) titanium dioxide with UV (TiO_2/UV)

- potential for both reductive and oxidative destruction pathways

3.5. Photochemical reactions

- photolysis limited to area where sunlight reaches (surface water, topsoil...)
- direct photolysis; light energy absorption by contaminants directly
- indirect photolysis;

  light energy transferred to intermediates (humic acids, iron oxides,...)

  -> oxygen or water to produce oxidants (hydroxyl radicals, singlet molecular oxygen,...)

  -> contaminants destruction

4. Biotic Transformations (p. 366)

4.1. Important organisms in hazardous waste systems

a) catabolism

- degradation vs. mineralization (CO_2, H_2O)
- energy for growth and motility (but not always!)

b) anabolism

- incorporation into cell biomass

c) bacteria and fungi

. *Pseudomonas, Bacillus, Arthrobacter...*

. Actinomycetes; *Nocardia, Mycobacterium*

d) methanogens
- strict anaerobes
- convert fermentation products (ethanol, acetate,...) to methane

CH_3COOH (EtOH) --> $\underline{CH_4}$ + CO_2

- also use hydrogen as an energy source

CO_2 + $4H_2$ --> $\underline{CH_4}$ + $2H_2O$

- text p. 368; "Methanogens are important ..... organic compounds"
  -> **WRONG!!!**

e) methanotrophs
- obligate aerobic
- low (or broad) specificity of methane monooxygenase (MMO)

CH_4 + $2O_2$ --> $\underline{CO_2}$ + $2H_2O$

- **cometabolically degrade** (oxidize) some chlorinated alkenes (e.g., PCE, TCE) and alkanes

f) a single species vs. a bacterial consortium (in degradading contaminants)

◎ Cometabolism

. fortuitous metabolism

. degraded *just because of being there* during the course of mineralization of other compound

. no nutritional benefit from the substrates cometabolized
-> no population growth observed

. parent compounds disappeared and cometabolic products accumulated in pure culture...but, in nature maybe different...

4.2. Fundamentals of microbial growth and metabolism

a) bacterial classification
- carbon source; autotroph vs. heterotroph
- energy source; chemotroph vs. phototroph

b) xenobiotics
- foreign chemicals
- standard catabolic pathways not exist
- degradation rates; xenobiotics < glucose < hydrocarbons

c) enzymes
- proteins made up of amino acids; three dimensional structure
- catabolic properties; degrade contaminants
- lower activation energy for degradation; rapid reaction
- active sites; biological redox reactions occur
- substrate-specific; "lock-and-key mechanism"
- conservative and can be used over and over

d) terminal electron acceptor (TEA)
- TEA that provides the greater free energy is favored
- free energy available ∝ redox potential
- $O_2 > NO_3^- > SO_4^{2-} > CO_2$
- aerobic (oxygen-consuming), denitrifying (nitrate reduction), sulfidogenic (sulfate reduction), methanogenic (methane-producing) conditions

e) oxidized organic compounds (i.e, chlorinated aliphatics; CCl_4, PCE,...) can serve as electron acceptors

f) fermentation
- internally balanced redox reaction
- produced organic acids, alcohols, ketones

4.3. Biodegradation reactions and pathways of hazardous contaminants

- basic strategy;
  . degrade large contaminants outside the cells (by exoenzymes)
  . take the small molecules into the cell (passive diffusion, active transport)
  . transform (mineralize) them to obtain energy (e.g., TCA cycle; Fig. 7.9)
- biochemical transformation reactions (Table 7.8)
  ; substitution, oxidation, reduction, dehydrohalogenation...

1) Aliphatic hydrocarbons

a) reduced carbons -> degraded more efficiently under aerobic conditions

b) biodegradation vs. chain length
- < C_{10} alkanes; toxicity is a factor
  (more toxic to microbes due to high water solubility)
- > C_{10} alkanes; high degree of sorption is a factor
  (due to low water solubility)

c) alkane biodegradation through dehydrogenase reactions
- alcohol->aldehyde->carboxylic acid->β-oxidation (C2 removal)(Fig.7.11)

d) branched aliphatics; at branching point, C1 removal should occur (α-oxidation)

* microbiologically, β-oxidation is easier to occur than α-oxidation
  --> explains why branched aliphatics are more recalcitrant in the environment

2) Benzene and PAHs

a) degradation pathways
- dioxygenase-catalyzed hydroxylation
  -> '-diol' produced -> ring cleavage... (Fig. 7.12 & Fig. 7.13)

b) biodegradability; function of the number of ring
- more than 4 rings -> highly hydrophobic -> highly sorptive
  -> biologically recalcitrant...(maybe not chemically!!!)
- anaerobic biodegradation; not common but reported for one- to three-ring aromatics under denitrifying, sulfate-reducing, methanogenic conditions

3) Halogenated solvents

a) three possible degradation pathways

- aerobic metabolism (contaminants used as an E source)
- aerobic cometabolism (by MMO)
- reductive dehalogenation (used as E acceptors); Fig. 7.14
  . primary anaerobic degradation mechanism
  . PCE -> TCE -> *cis*-1,2-DCE -> vinyl chloride -> ethylene
  . VC; more toxic than PCE, TCE
  . if combined with aerobic process, completely mineralized to CO_2, H_2O

b) degradation pathway is determined by the oxidation state of C

- reduced compounds (e.g. 1,2-dichloroethane, methylene chloride...)
  ; aerobically oxidized
- oxidized compounds; carbon tetrachloride, PCE, TCE...
  ; degraded by reductive processes

c) cometabolic degradation

- methylene chloride, chloroform, TCA (trichloroacetic acid);
  cometabolically degraded by *Nitrosomonas* (NH_4^+ -> NO_2^-)
- reduced organic compounds (acetate, propane, phenol. toluene...)
  serve as the energy source (also electron donor) for cometabolism of TCE (electron acceptor) -> reductive dehalogenation

d) during reductive dehalogenation, nitrate, sulfate can compete with halogenated aliphatics for electrons (both are electron acceptors!!!)

- evaluation of electron acceptors determined by redox potentials
- Table 7.9
- Example 7.7

If acetate is the electron donor, evaluate the thermodynamic potential for the reductive dehalogenation of chloroform in the presence of sulfate.

(solution)

$CHCl_3 + H^+ + 2e^- \rightarrow CH_2Cl_2 + Cl^-$ $\quad E^0 = +0.56$

$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-$ $\quad E^0 = +0.40$

`

$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$ $\quad E^0 = -0.22$

$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ 8e^-$ $\quad E^0 = +0.40$

E^0 for chloroform-acetate +0.96V vs. E^0 for acetate-sulfate +0.18V

--> *chloroform will be reduced* rather than sulfate (**no competition!**)

4) Pesticides

- DDT (Fig. 7.15); 2,4-D (Fig. 7.16)

5) Polychlorinated biphenyls (PCBs)

- lower PCBs; aerobically biodegradable
- higher PCBs; reductive dehalogenation

5. Common Themes and Perspectives in Abiotic and Biotic Transformations (p. 386)

1) What's the difference between abiotic and biotic transformation?
   a) reaction thermodynamics are the same
      - oxidized chemicals degraded by reduction, and vice versa
      - Table 7.10
   b) main difference; enzymatic catalysis
   c) abiotic catalysis reaction or similar one? (p. 365)
   d) **exception:** highly chlorinated alkenes and aromatics with hydroxyl radicals
      - PCE, hexachlorobenzene, hexachlorocyclopentadiene,...
      - probably due to electron-rich π bonds of alkenes and aromatics that are still available to react with hydroxyl radicals
2) Limitations and Applications
   a) potential biotic and abiotic transformation mechanisms may not work or not be executed properly in the environment (due to the interactions with the env.)
   -> persistent, recalcitrant contaminants formed!!!
   b) engineered remediation technologies using the known transformation mechanisms (either biotic or abiotic; Table 7.11)

6. Measurement of Transformation Rates (p. 389)

1) Bioassessment (biotreatability) study
   a) to determine whether contaminants at a site are biodegradable
      - the number of microorganisms
      - whether the indigenous microorgannisms will biodegrade the contaminants
      - the rate at which they are degradaded
      - the identity of the biodegradation products (toxic intermediates?)
   b) use an unaugmented system
      - environmental conditions; temp, pH, nutrients, moisture...
      - to determine the degradation ability of indigenous population
   c) biotreatability study
      - test augmented systems for bioremmediation process design
        . add appropriate bacteria (bioaugmentation)
        . add nutrients (biostimulation)
        . add cometabolites (e.g., methane, phenol,...)
        . add terminal electron acceptors
   d) biometry flask system (Fig. 7.19)
      - respirometer (O_2 consumption - CO_2 evolution)
      - CO_2 trapped in an alkali solution (e.g., NaOH, KOH) -> CO_3^{2-}
      - at alkali pH, CO_2 dissoves as CO_3^{2-}
        at low pH, CO_2 form dominates (-> volatile -> loss!!!)

▣ Kinetics and Arrhenius Equation

1. Kinetics

Zero Order Reaction

A reaction is of zero order when the rate of reaction is independent of the concentration of materials. The rate of reaction is a constant. When the limiting reactant is completely consumed, the reaction stops abruptly.

The zero order rate law for the general reaction

$$\mathbf{A \rightarrow P}$$

is written as the equation

$$-\frac{\mathbf{d[A]}}{\mathbf{dt}} = \mathbf{k} \qquad (1)$$

which on integration of both sides gives

$$\mathbf{[A]} = -\mathbf{kt} + \mathbf{C} \qquad (2)$$

When $\mathbf{t = 0}$ the concentration of **A** is $\mathbf{[A]_0}$. The constant of integration must be $\mathbf{[A]_0}$.

Now the integrated form of zero-order kinetics can be written as follows

$$\mathbf{[A]} = -\mathbf{kt} + \mathbf{[A]_0} \qquad (3)$$

Plotting [A] versus t will give a straight line with slope -k.

First Order Reaction

A general unimolecular reaction

$$\mathbf{A \rightarrow P}$$

where **A** is a reactant and **P** is a product is called a first-order reaction.

The rate is proportional to the concentration of a single reactant raised to the first power.

The decrease in the concentration of **A** over time can be written as:

$$\mathbf{v} = -\frac{\mathbf{d[A]}}{\mathbf{dt}} = \mathbf{k[A]} \qquad (1)$$

$$-\frac{\mathbf{d[A]}}{\mathbf{[A]}} = \mathbf{k\,dt} \qquad (2)$$

Equation **(2)** represents the differential form of the rate law. Integration of this equation and determination of the integration constant **C** produces the corresponding integrated law.

Integrating equation **(2)** yields:

$$\ln[A] = -kt + C \qquad (3)$$

The constant of integration **C** can be evaluated by using boundary conditions. When **t = 0**, **[A] = $[A]_0$**. $[A]_0$ is the original concentration of **A**.

Substituting into equation **(3)** gives:

$$\ln[A]_0 = -k(0) + C \qquad (4)$$

Therefore the value of the constant of integration is:

$$C = \ln[A]_0 \qquad (5)$$

Substituting **(5)** into **(4)** leads to:

$$\ln\frac{[A]}{[A]_0} = -kt \qquad (6)$$

Plotting ln[A] or ln[A] / $[A]_0$ against time creates a straight line with slope -k. The plot should be linear up to a conversion of 80-90%, that is up to the point at which 80-90% of the concentration of the reactant is consumed.

Equation **(6)** can also be written as:

$$[A] = [A]_0 e^{-kt} \qquad (7)$$

This means that the concentration of **A** decreases exponentially as a function of time.

The rate constant **k** can also be determined from the half-life $t_{1/2}$. Half-life is the time it takes for the concentration to fall from $[A]_0$ to $[A]_0 / 2$.

According to equation **(6)** is obtained:

$$k\,t_{1/2} = \ln\frac{[A]_0}{[A]_0/2} \quad \text{or} \quad k = \frac{\ln 2}{t_{1/2}} \qquad (8)$$

Pseudo First Order Reaction

A and **B** react to produce **P**:

$$A + B \rightarrow P$$

If the initial concentration of the reactant **A** is much larger than the concentration of **B**, the concentration of **A** will not change appreciably during the course of the reaction The concentration of the reactant in excess will remain almost constant. Thus the rate's dependence on **B** can be isolated and the rate law can be written

$$v = -\frac{d[B]}{dt} = k' \cdot [B] \quad \text{where} \quad k' = k \cdot [A] \qquad (1)$$

Equation **(1)** represents the differential form of the rate law. Integration of this equation and evaluation of the integration constant **C** produces the corresponding integrated law.

Substituting **[B] = c** into equation **(1)** yields:

$$-\frac{dc}{c} = k' \cdot dt \qquad (2)$$

Integrating equation **(2)** gives:

$$\ln c = -k' \cdot t + C \qquad (3)$$

The constant of integration **C** can be evaluated by using boundary conditions. At **t = 0** the concentration of **B** is c_0.

Therefore

$$C = \ln c_0 \qquad (4)$$

Accordingly is obtained:

$$\ln c = \ln c_0 - k' \cdot t \quad \text{or} \quad c = c_0 \cdot e^{-k' \cdot t} \qquad (5)$$

If the decrease in concentration of **B** is followed by photometric measurement the **Beer' Law** must be taken into account.

Combining equation **(4)** and **Beer' Law**

$$A = \log \frac{P_0}{P} = -\log T = \varepsilon \cdot c \cdot d \qquad (6)$$

A = absorbance, e = molar absorbtivity with units of $L \cdot mol^{-1}$ cm^{-1}
c = concentration of the compound in solution, expressed in $mol \cdot L^{-1}$
P_0= radiant power for radiation entering; P= radiant power for radiation leaving

gives the relationship between **k'** and **lnA**:

$$\ln A = -k' \cdot t + \ln c_0 + \ln(\varepsilon \cdot d) \quad \text{or} \quad \ln A = -k' \cdot t + C \qquad (7)$$

One needs only monitor the relative concentration of **B** as a function of time to obtain the **pseudo-first order rate constant k'**. The value of **k'** can then be divided by the known, constant concentration of the excess compound to obtain the true constant second order **k**:

$$k = \frac{k'}{[Ar]} \qquad (8)$$

The **pseudo-first order rate constant k'** can be also determined from the **half-life** $t_{1/2}$.

$$k' \cdot t_{1/2} = \ln \frac{c_0}{c_0 / 2} \quad \text{or} \quad k' = \frac{\ln 2}{t_{1/2}} \qquad (9)$$

Second Order Reaction

The rate of a second order reaction is proportional to either the concentration of a reactant squared, or the product of concentrations of two reactants.

For the general case of a reaction between **A** and **B**, such that

$$A + B \rightarrow P$$

the rate of reaction will be given by

$$-\frac{d[A]}{dt} = k \cdot [A][B] \qquad (1)$$

1. Initial concentrations of the two reactants are equal:

Equation **(1)** can be written as:

$$-\frac{d[A]}{dt} = k \cdot [A]^2 \qquad (2)$$

Separating the variables and integrating gives:

$$\frac{1}{[A]} = kt + C \qquad (3)$$

With the condition that $[A] = [A]_0$ at $t = 0$ the constant of integration C becomes equal to $1 / [A]_0$.

Thus the second order integrated rate equation is

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \qquad (4)$$

A plot of $1 / [A]$ vs t produces a straight line with slope k and intercept $1 / [A]_0$. The plot should be linear up to a conversion of 50%, that is up to the point at which 50% of the reactant concentration is consumed.

2. Starting concentrations of the two reactants are different:

If $[A]_0$ and $[B]_0$ are different the variable **x** is used.

Equation **(1)** becomes

$$\frac{dx}{([A]_0 - x)([B]_0 - x)} = kdt \qquad (5)$$

where $[A]_0 - x = [A]$, $[B]_0 - x = [B]$ and **x** is the decrease in the concentration of **A** and **B**.

Taking into account that the left side can be written as

$$\frac{1}{[B]_0 - [A]_0}\left(\frac{1}{[A]_0 - x} - \frac{1}{[B]_0 - x}\right) \qquad (6)$$

Integrating equation **(5)** gives

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0 - x}{[B]_0 - x} = kt + C \qquad (7)$$

where **C** is the constant of integration.

Using the condition that **x = 0**, when **t = 0**, the value of **C** can be found

$$C = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0}{[B]_0} \qquad (8)$$

and equation **(7)** becomes

$$\ln \frac{[A]_0 - x}{[B]_0 - x} = kt\,([B]_0 - [A]_0) + \ln \frac{[A]_0}{[B]_0} \qquad (9)$$

A plot of

$$\ln \frac{[A]_0 - x}{[B]_0 - x} \qquad (10)$$

against **t** should be a straight line.

If the experimental method yields reactant concentrations rather than **x**, the equivalent form of the equation is

$$\ln \frac{[B]_0\,[A]}{[A]_0\,[B]} = kt\,([B]_0 - [A]_0) \qquad (11)$$

If equimolar amounts of **A** and **B** are converted, then **[A]** can be expressed by the concentration of **B**.

If **[B] = x** , **$[A] = [A]_0 - (x_0 - x)$**

Provided that the initial concentration of **A** is twice the concentration of **B** equation **(11)** becomes

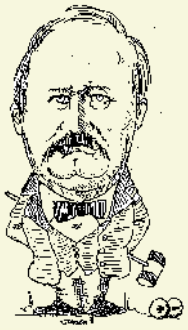
$$\ln\left[\frac{1}{2}\left(\frac{x_0}{x} + 1\right)\right] = x_0 \cdot kt \qquad (12)$$

Summary

Reaction Order	Differential Rate Law	Integrated Rate Law	Linear Plot	Slope of Linear Plot	Units of Rate Constant
0	$-d[A]/dt = k$	$[A] = [A]_0 - kt$	[A] vs t	- k	$mol \cdot L^{-1} \cdot s^{-1}$
1st	$-d[A]/dt = k[A]$	$[A] = [A]_0 e^{-kt}$	ln[A] vs t	- k	s^{-1}
2nd	$-d[A]/dt = k[A]^2$	$1/[A] = 1/[A]_0 + kt$	1/[A] vs t	k	$L \cdot mol^{-1} \cdot s^{-1}$

2. Arhenius Equation

Arrhenius Equation



Svante Arrhenius

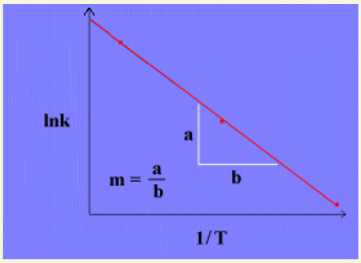
It is a well-known fact that raising the temperature increases the reaction rate. Quantitatively this relationship between the rate a reaction proceeds and its temperature is determined by the Arrhenius Equation:

$$k = A\, e^{-\frac{E_a}{RT}} \qquad (1)$$

E_a = activation energy
R = 8.314 J/mol·K
T = absolute temperature in Kelvins
A = frequency factor

The Arrhenius equation is often written in the logarithmic form:

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (2)$$



Determination of E_a

A plot of **lnk** versus **1/T** produces a straight line, from which the activation energy, E_a, can be determined because the slope is - E_a/ R.

The y-intercept represents the value for **lnA**.

An accurate determination of the activation energy requires at least three runs completed at different reaction temperatures.

"Two-Point" Arrhenius Equation

The "Two-Point" Equation provides a computational method to determine the activation energy for a given reaction from the experimental data found at two different reaction temperatures. The Arrhenius equations for two temperatures (T_1 and T_1) give two rate constants (k_1 and k_1):

at T_1: $$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

at T_2: $$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Combining the two Arrhenius equations yields

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (3)$$

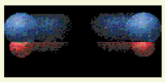
$$E_a = \frac{R\, T_1\, T_2}{(T_1 - T_2)} \ln \frac{k_1}{k_2} \qquad (4)$$

Henry Eyring

Both the **Arrhenius** and the **Eyring equation** describe the temperature dependence of reaction rate. In the strict sense, the **Arrhenius equation** may be applied only to gas reactions. The **Eyring equation** is used in gas, condensed and mixed phase reactions - all places where the simple **collision model** is not very helpful. The Arrhenius equation is founded on the empirical observation, that raising the temperature increases the rate of reaction. The **Eyring equaion** is a theoretical construct, based on **transition state** model.

According to the **'transition state theory'** during a chemical reaction the reactants are getting over into an unsteady intermediate state.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^{\#} \xrightarrow{k_2} C \quad (1)$$



Effective collision
Online Introductory Chemistry

When two particles **A** and **B** collide, due to collision energy a complex is formed. If the collision involves more than a certain amount of energy ('threshold energy'), the **'activated complex'** or **'transition state'** $AB^{\#}$ is formed, an unstable arrangement, in which bonds break and form to generate the products **C** or to degenerate back to the reactants **A** and **B**.

The concentration change of the complex $AB^{\#}$ can be described as follows:

$$\frac{d[AB^{\#}]}{dt} = k_1 \cdot [A] \cdot [B] - k_{-1} \cdot [AB^{\#}] - k_2 \cdot [AB^{\#}] \quad (2)$$

Due to the equilibrium between the 'activated Complex' $AB^{\#}$ and the reactants **A** and **B**, the components $k_1 \cdot [A] \cdot [B]$ and $k_{-1} \cdot [AB^{\#}]$ cancel out. Thus the reaction rate is directly proportional to the concentration of $AB^{\#}$:

$$-\frac{d[AB^{\#}]}{dt} = k_2 \cdot [AB^{\#}] \quad (3)$$

k_2 is given by statistical mechanics:

$$k_2 = \frac{k_B \cdot T}{h} \quad (4)$$

k_B = Boltzmann's constant [$1.381 \cdot 10^{-23}$ J · K^{-1}]
h = Plank constant [$6.626 \cdot 10^{-34}$ J · s]

k_2 is called **'universal constant for a transition state'** (~ $6 \cdot 10^{-12}$ sec^{-1} at room temperature).

Additionally $[AB^{\#}]$ can be derived from the quasi stationary equilibrium between $AB^{\#}$ and **A**, **B** by applying the mass action law:

$$[AB^{\#}] = K^{\#} \cdot [A] \cdot [B] \quad (5)$$

$K^{\#}$ = **thermodynamic equilibrium constant**

Due to the equilibrium that will be reached rapidly, the reactants and the activated complex decrease at the same rate. Therefore, considering both **equation (4)** and **(5)**, **equation (3)** become:

$$-\frac{d[AB^{\#}]}{dt} = \frac{k_B \cdot T}{h} \cdot K^{\#} \cdot [A] \cdot [B] \quad (6)$$

With consideration of the derived rate laws and by algebraic rearrangement, **equation (6)** can be rewritten:

$$k = \frac{k_B \cdot T}{h} \cdot K^{\#} \quad (7)$$

Additionally thermodynamics gives a further representation of the equilibrium constant:

$$\Delta G^{\#} = -R \cdot T \cdot \ln K^{\#} \quad (8)$$

$$\Delta G^{\#} = \Delta H^{\#} - T \cdot \Delta S^{\#} \quad (9)$$

$\Delta G^{\#}$ = free activation enthalpy [kJ · mol^{-1}]
$\Delta S^{\#}$ = activation entropy [J · mol^{-1} · K^{-1}]
$\Delta H^{\#}$ = activation enthalpy [kJ · mol^{-1}]

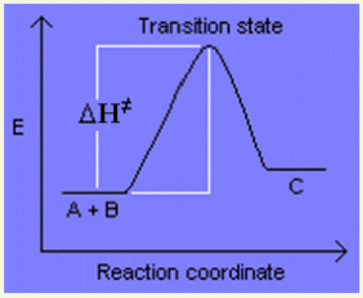


Figure 1: Energy profile
E: Potential energy
Reaction coordinate: Bond length or bond angle
Transition state: Maximum of energy in the path way,
i.e. along the reaction coordinate

H is the amount of heat of a system with constant pressure. **$\Delta H^{\#}$** is the enthalpy difference between the activated complex and the reactants **A** and **B**. It is called **activation enthalpy** (**Fig. 1**).
S is for the entropy, the extent of randomness or disorder in a system. The entropy difference between activated complex and the reactants is called **activation entropy $\Delta S^{\#}$**.
$\Delta G^{\#}$ is the **free activation enthalpy**. According to **equation (9)** **$\Delta G^{\#}$** is **molar enthalpy $\Delta H^{\#}$ minus the product of the temperature T** (which is in kelvin) and the **change in entropy $\Delta S^{\#}$**. The general rule applies: A stabilization of the activated complex reduces the enthalpy difference **$\Delta G^{\#}$** and increases the rate.
$\Delta G^{\#}$ represents the determining driving power for a reaction. The sign of **$\Delta G^{\#}$** determines if a reaction is spontaneous or not.

$\Delta G^{\#} < 0 \Rightarrow$ reaction is spontaneous
$\Delta G^{\#} = 0 \Rightarrow$ system at equilibrium, no net change occurs
$\Delta G^{\#} > 0 \Rightarrow$ reaction is not spontaneous

Combining **Equation (8)** and the expression **(9)** and solving for **lnk** yields:

$$\ln K^{\#} = -\frac{\Delta H^{\#}}{R \cdot T} + \frac{\Delta S^{\#}}{T} \quad (10)$$

The ***Eyring equation***: is found by substituting **equation (10)** into **equation (7)**:

$$k = \frac{k_B \cdot T}{h} \cdot e^{-\frac{\Delta H^{\#}}{R \cdot T}} \cdot e^{\frac{\Delta S^{\#}}{R}} \quad (11)$$

Equation (11) is transformed into a linear expression:

$$\ln k = \ln \frac{k_B}{h} \cdot T - \frac{\Delta H^{\#}}{R} \cdot \frac{1}{T} + \frac{\Delta S^{\#}}{R} \quad (12)$$

$$\ln \frac{k}{T} = -\frac{\Delta H^{\#}}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^{\#}}{R} \quad (13)$$

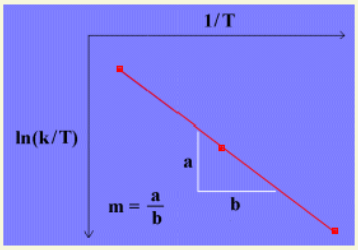


Figure 2: Determination of $\Delta H^{\#}$

A plot of **ln(k/T)** versus **1/T** will be a straight line with a slope of **m** = - $\Delta H^{\#}$/ R (**Fig. 2**). $\Delta H^{\#}$ can be calculated from the slope of this line. **Multiplying -m by -R (-8.314J/mol·K) yields** $\Delta H^{\#}$.

Using the y-intercept

$$y(x = 0) = \ln \frac{k_B}{h} + \frac{\Delta S^{\#}}{R} \quad (14)$$

$\Delta S^{\#}$ can be determined and thus is enabled the calculation of $\Delta G^{\#}$ for the appropriate reaction temperatures according to **equation (9)**.

A comparison between the Arrhenius equation and the ***Eyring equation*** shows, that E_a and $\Delta H^{\#}$ or **lnA** and $\Delta S^{\#}$ are analog quantities. For mechanistical investigations the different activation parameters E_a / **lnA** or $\Delta H^{\#}$ / $\Delta S^{\#}$ are used alternatively. The activation energy E_a is not exactly equal to the activation enthalpy $\Delta H^{\#}$, but is greater than it by a small amount (the difference is R·T).

- **Small values of E_a and $\Delta H^{\#}$ $\Rightarrow$ fast rate**
- **large values of E_a and $\Delta H^{\#}$ $\Rightarrow$ slow rate**
- **lnA small, corresponding to very negative values of $\Delta S^{\#}$ $\Rightarrow$ slow rate**
- **lnA large, corresponding to relatively positive values of $\Delta S^{\#}$ $\Rightarrow$ fast rate**

Typical values for E_a and $\Delta H^{\#}$ run from 20 to 150 [kJ / mol].

The study of the temperature dependence supplies the above all mechanistically important values lnA or $\Delta S^{\#}$, equivalent in their predicate strength.

- **lnA small, corresponding to very negative values of $\Delta S^{\#}$ (unfavorable)**

The transition state is highly ordered in comparison to the ground state. This is generally the case, if on the way to the transition state, degrees of freedom (translational, rotational or vibrational) are frozen.

- **lnA large, corresponding to relatively positive values of $\Delta S^{\#}$ (favorable)**

In comparison to the ground state the transition state is disordered. Translational, rotational or vibrational degrees of freedom are set free.

lnA and $\Delta S^{\#}$ are sensible sensors for the status order of transition state.

Note:
Although the determination of the activation parameters must be performed accurately, it may not pretend an excessive accuracy. The values of the activation energy and activation enthalpy are rounded in publications to one decimal place. The value of activation entropy is to be specified basically with whole numbers. Values of entropies $\Delta S^{\#} < \pm 10$ are written to one decimal place of accuracy. The value of lnA shall be expressed with an accuracy of two decimal places.
An accurate determination of the activation energy requires at least three runs completed at different reaction temperatures. If the data points in the plot of ln(k/T) versus 1/T (Fig. 2) do not lie exactly on a straight line, a linear regression analysis providing the 'line of best fit' will not increase the accuracy. If the plotted points deviate significantly from the straight line, the rate constant should be determined at a further reaction temperature, since each of the three data points can be false. Basically, it recommends to increase the accuracy of the measured values by improvement of the measuring method (accurate thermostating of reaction solutions).
Sometimes the data points are positioned on a concave or convex curve. Most notably a secondary reaction is responsible for this behavior. The secondary reaction will have more or less importance, owing to the deviation of activation parameters with rising temperature. In this case the calculation of the activation parameters is senseless.