Advanced Water Quality

Class 6: Reaction Kinetics

Effect of Temperature on K_{eq} Values

- Relationship between K_{eq} and ΔG^0 valid **<u>only</u>** at standard T, P

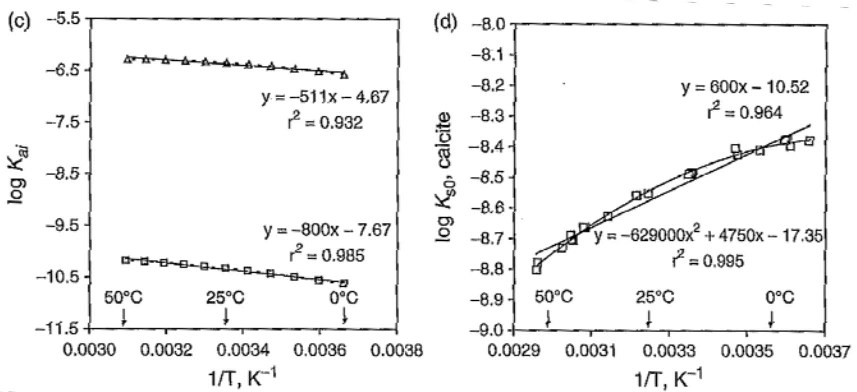
$$\xcancel{\ln K_{eq} = -\frac{\Delta G^0}{RT}}$$

Account for effects of varying temperature using Van't Hoff Equation

$$\ln\left(\frac{K_{eq,T2}}{K_{eq,T_{std}}}\right)=\frac{\Delta H^0}{R}\left(\frac{1}{T_{std}}-\frac{1}{T_2}\right)=\frac{\Delta H^0(T_2-T_{std})}{RT_{std}T_2}$$

- Obtain ΔH^0 similar to ΔG^0, using values in Appendix of your text

$$\Delta H^0=\left(\sum_i \upsilon_i H^0_{f,i}\right)_{PRODUCTS}-\left(\sum_i \upsilon_i H^0_{f,i}\right)_{REACTANTS}$$



Account for effects of varying ionic strength using activity coefficients estimated with Davies Eq.

$$K_{eq}=\frac{\{H_2CO_3\}^1}{\{H^+\}^2\{CO_3^{2-}\}^1}$$

$$=\frac{(\gamma_{H_2CO_3}[H_2CO_3])^1}{(\gamma_{H^+}[H^+])^2(\gamma_{CO_3^{2-}}[CO_3^{2-}])^1}$$

Davies

Applicable at $I < 0.5\ M$

$$\log\gamma_{\text{Davies}}=-Az^2\left(\frac{I^{1/2}}{1+I^{1/2}}-0.2I\right)$$

Today’s learning objectives

- Introduce kinetics models
- Identify common empirical rate laws and diagnostic plots of data for each
- Convert rate constants to characteristic times for reaction
- Learn to correct for temperature effects on reaction kinetics.

Reaction Kinetics

- Kinetics
  - how fast?
    - central question to environmental fate and transport prediction
  - what mechanism?
    - Predicting fate of compound in diverse environments
    - Designing remediation techniques
  - Kinetics models
    - What is the effect of reactant concentration on reaction rates?
    - What is the effect of temperature
    - What is the effect of different solution conditions (e.g., pH)

Factors that Affect Reaction Rates

pH

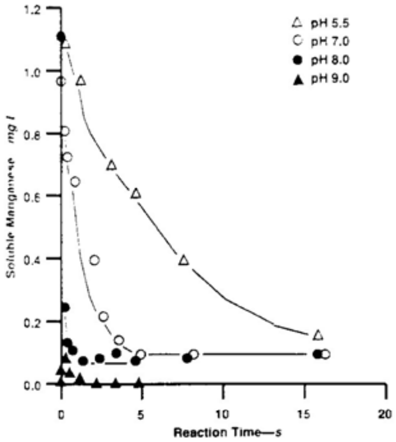


Figure 3. Effect of solution pH on Mn(II) oxidation by potassium permanganate *(temperature = 25°C; DOC <1 mg/L; target pH values listed in figure)*

Temp

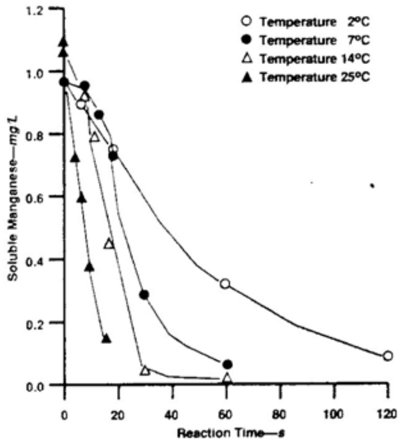


Figure 4. Effect of solution temperature on Mn(II) oxidation by potassium permanganate *(DOC <1 mg/L; target pH = 5.5)*

Other Constituents (e.g., DOC)

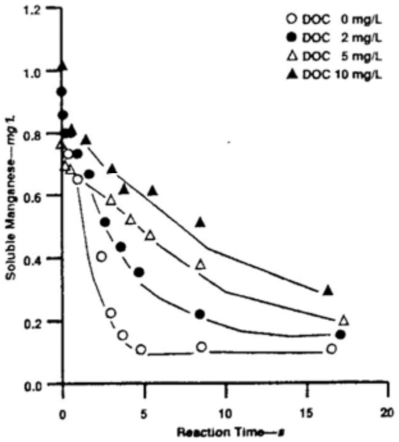
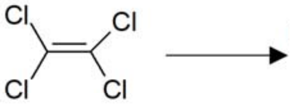


Figure 5. Mn(II) oxidation by potassium permanganate in the presence of different concentrations of Thousand Acre fulvic acids *(temperature = 25°C; target pH = 7.0)*

Use of Metallic Iron (Fe^0) Permeable Barrier Walls to Degrade Organochloride Compounds (e.g., solvent contaminants)



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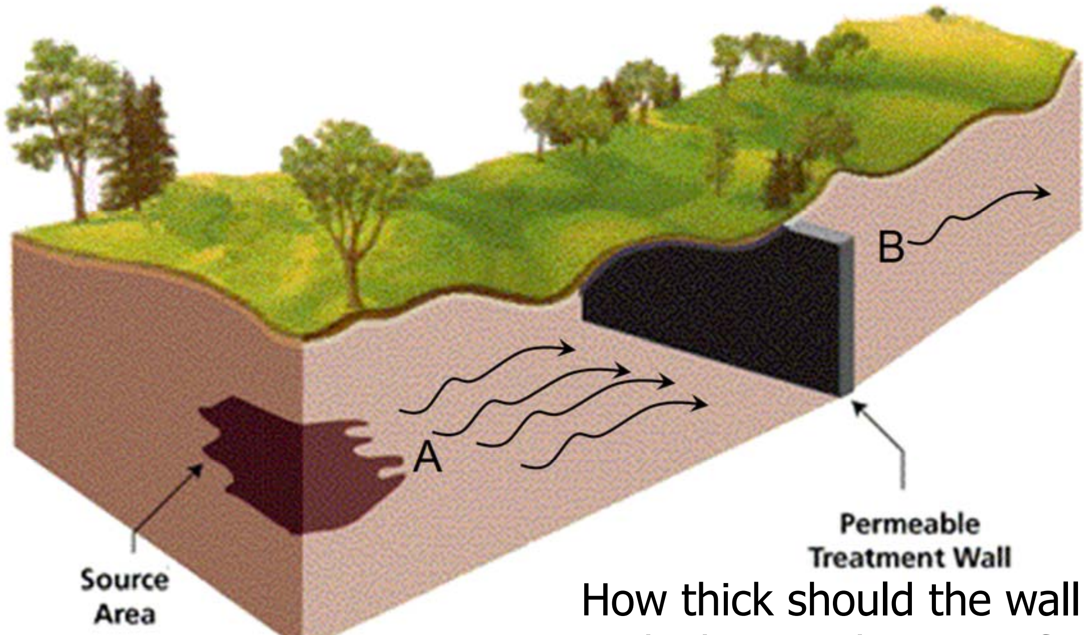

How thick should the wall be, and what products are formed?

Kinetics

- Empirical Rate Laws
  - Differential rate laws describe the effects of individual reactant concentrations on rxn rate

$$4Fe(II) + O_2 + 4H^+ \longrightarrow 4Fe(III) + 2H_2O$$

$$\frac{d[Fe(II)]}{dt} = -k[Fe(II)][O_2][OH^-]^2$$

  - Reaction is 1st-order in [Fe(II)], 1st order in $[O_2]$, 2nd-order in $[OH^-]$ and 4th order overall
  - CANNOT DETERMINE RATE LAW FROM REACTION STOICHIOMETRY (must be determined experimentally)
  - Integrated rate laws: written in terms of reactant concentrations and time only

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First-order rate law: A → B

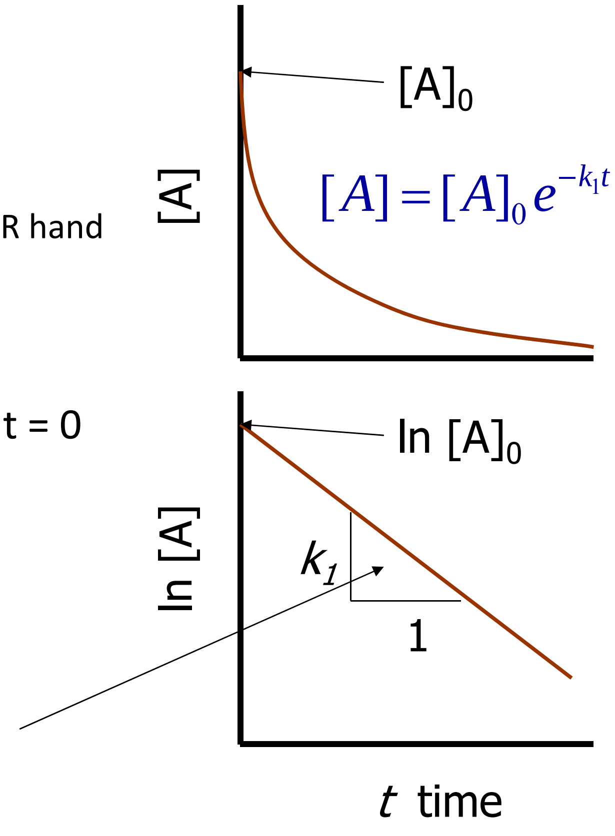
$$\frac{d[A]}{dt} = -k_1[A]$$

*k_1 has units of (s^{-1}) to balance L & R hand side of rate law expression

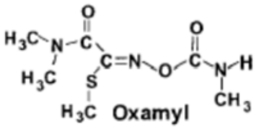
- Separate [A] and t terms, and integrate from $[A]_0$ to [A] and t = 0 to t:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_{t=0}^{t} -k_1 dt$$

$$\ln[A] = \ln[A]_0 - k_1 t$$



Problem 1: Degradation of the pesticide oxamyl in groundwater can be described by a first-order rate law, with rate constant of 3×10^{-3} h^{-1} at pH 7 and 25°C. If the groundwater initially contains 2 mg/L oxamyl, determine how long it will take before the compound degrades to the MCL value of 0.2 mg/L.



First-order rate law: Reaction Half Life

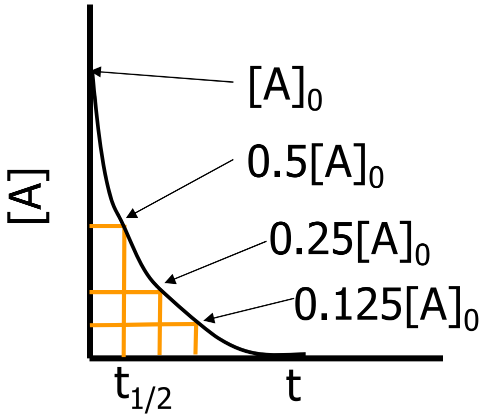
- first order
  - half-life, $t_{1/2}$
  - time to reduce $[A]_0$ by 50%; i.e., to $0.5[A]_0$

$$0.5[A]_0 = [A]_0 e^{-k_1 t}$$

$$0.5 = e^{-k_1 t}$$

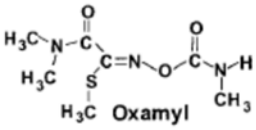
$$\ln 0.5 = -k_1 t$$

$$t_{1/2} = -\frac{\ln 0.5}{k_1} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$$



Successive $t_{1/2}$ equal for first-order rate law

Problem 2: Degradation the half life for the pesticide oxamyl:



Half life is only one “characteristic time” used for reactions. Others might include t90 (time for 90% loss) and t99 (time for 99% loss)

It is important to compare the characteristic timescale of reactions to water residence times

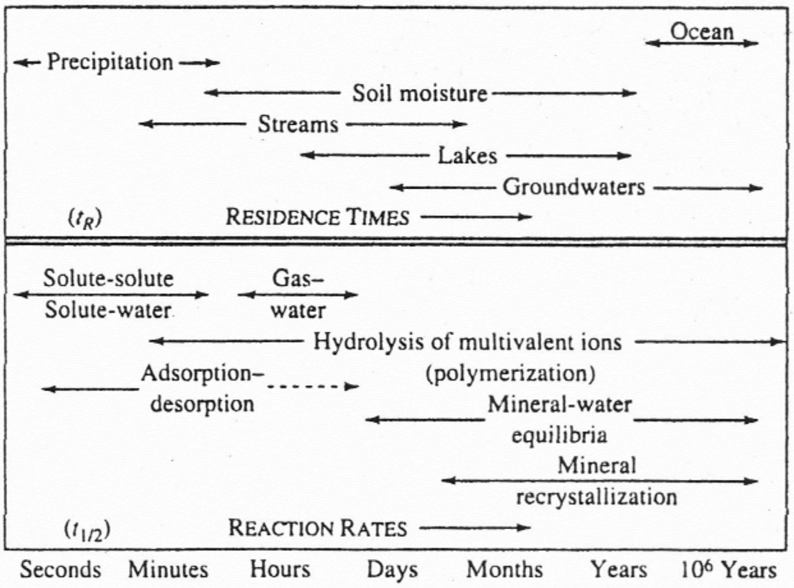


Figure 2.2 Schematic comparison between the half-times of some reaction types ($t_{1/2}$), and the residence times (t_R) of some waters in the hydrosphere. After Langmuir and Mahoney (1985). Reprinted from the National Water Well Assoc. Used by permission.

It is important to compare the characteristic timescale of reactions to water residence times

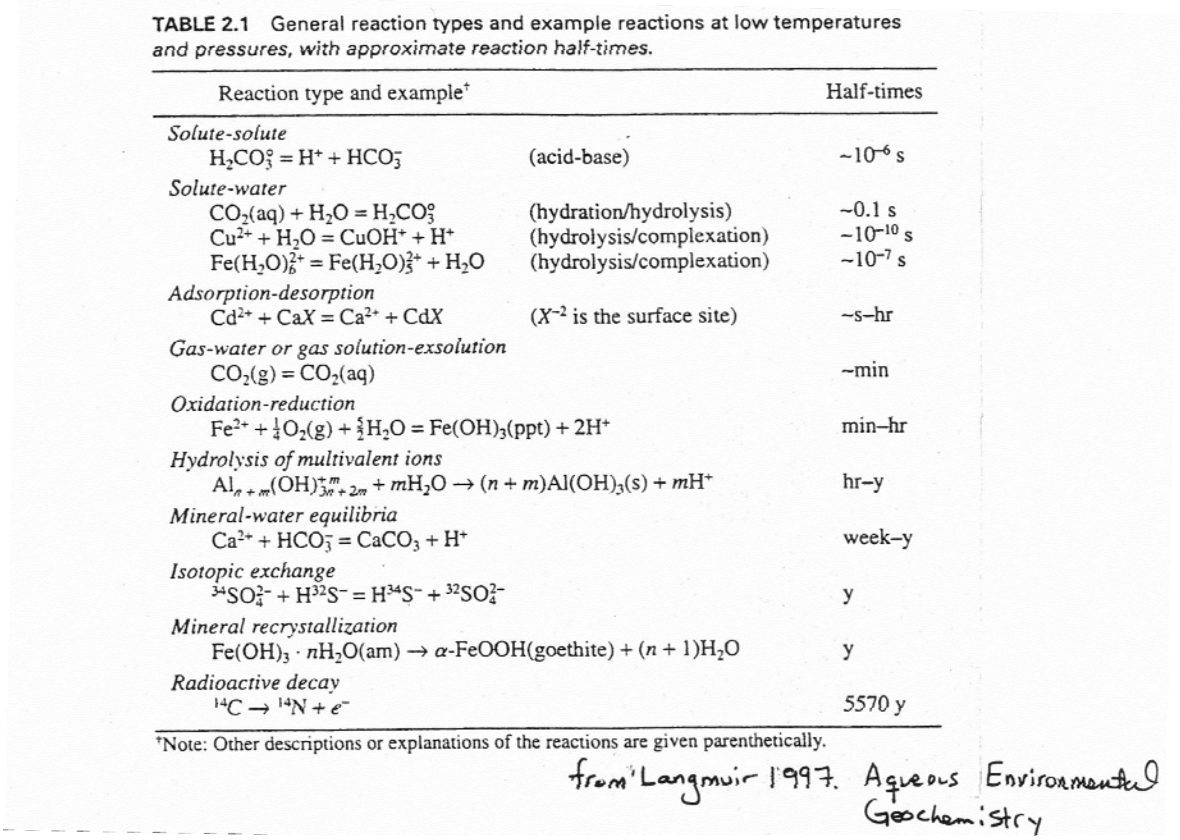


TABLE 2.1 General reaction types and example reactions at low temperatures and pressures, with approximate reaction half-times.

Reaction type and example†		Half-times
Solute-solute		
$H_2CO_3^\circ = H^+ + HCO_3^-$	(acid-base)	~10^{-6} s
Solute-water		
$CO_2(aq) + H_2O = H_2CO_3^\circ$	(hydration/hydrolysis)	~0.1 s
$Cu^{2+} + H_2O = CuOH^+ + H^+$	(hydrolysis/complexation)	~10^{-10} s
$Fe(H_2O)_6^{3+} = Fe(H_2O)_5^{2+} + H_2O$	(hydrolysis/complexation)	~10^{-7} s
Adsorption-desorption		
$Cd^{2+} + CaX = Ca^{2+} + CdX$	(X^{-2} is the surface site)	~s–hr
Gas-water or gas solution-exsolution		
$CO_2(g) = CO_2(aq)$		~min
Oxidation-reduction		
$Fe^{2+} + \frac{1}{4}O_2(g) + \frac{5}{2}H_2O = Fe(OH)_3(ppt) + 2H^+$		min–hr
Hydrolysis of multivalent ions		
$Al_{n+m}(OH)_{3n+2m}^{+m} + mH_2O \rightarrow (n+m)Al(OH)_3(s) + mH^+$		hr–y
Mineral-water equilibria		
$Ca^{2+} + HCO_3^- = CaCO_3 + H^+$		week–y
Isotopic exchange		
$^{34}SO_4^{2-} + H^{32}S^- = H^{34}S^- + {}^{32}SO_4^{2-}$		y
Mineral recrystallization		
$Fe(OH)_3 \cdot nH_2O(am) \rightarrow \alpha\text{-}FeOOH(goethite) + (n+1)H_2O$		y
Radioactive decay		
$^{14}C \rightarrow {}^{14}N + e^-$		5570 y

†Note: Other descriptions or explanations of the reactions are given parenthetically.

from Langmuir 1997. Aqueous Environmental Geochemistry

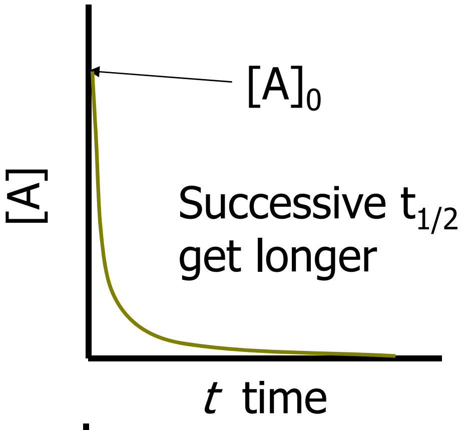
2nd-order rate law

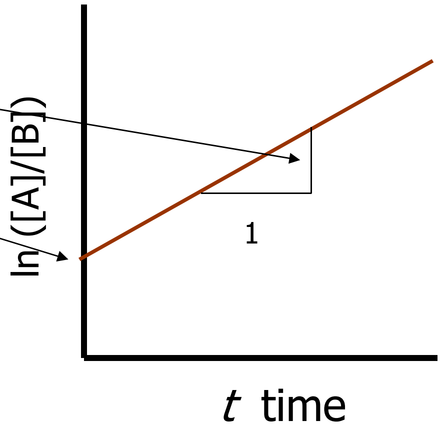
A + B → C

$$\frac{d[A]}{dt} = -k_2[A][B]$$

$$\ln\frac{[A]}{[B]} = \ln\underbrace{\frac{[A_o]}{[B_o]}} + k_2\underbrace{([A_o]-[B_o])}t$$

k_2 (M^{-1} s^{-1})





Zeroth-order rate law:

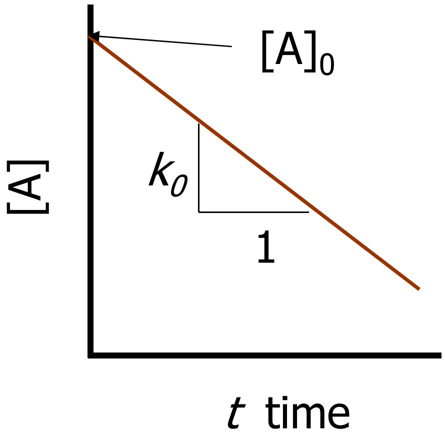
- Commonly observed when:
  - Influx of reactant from outside the system maintains a steady-state concentration
  - Limited reaction sites (e.g., on a surface or enzyme active site) is saturated.

$$\frac{d[A]}{dt} = -k_0[A]^0 = -k_0$$

Integration yields linear relationship between concentration and time

$$[\mathrm{A}] = [A]_0 - k_0 t$$

k_0 has units of (M s^{-1})

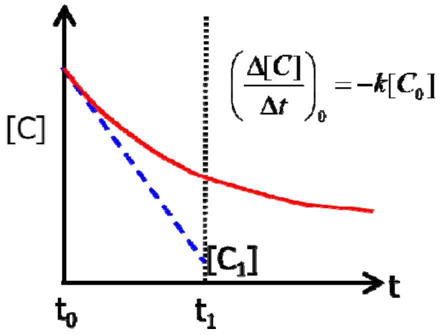


More complex rate laws

- Higher order rate laws are also possible, especially for complex, multi-step processes, e.g.,

$$\frac{d[A]}{dt} = -k_2[A][B][C] \qquad \frac{d[Fe(II)]}{dt} = -k[Fe(II)][O_2][OH-]^2$$

- However, for these rate laws, obtaining analytical solutions (i.e., the integrated rate expression) is not easy or possible in some cases.
  - Use numerical methods to solve
  - E.g., Runge-Kutta, Euler's method to approximate ΔC/Δt



Pseudo-First-Order Rate Law

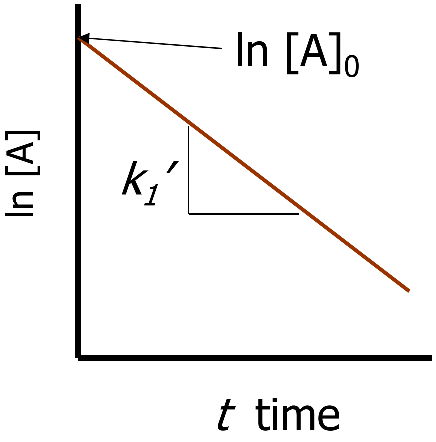
- Second-order reactions pretend to be first-order if the concentration of one reactant remains roughly constant during the reaction
    - [B] >> [A]
    - Constant source of [B] production

$$\frac{d[A]}{dt} = -\overbrace{k_2[\mathrm{B}]}^{k_1'}[\mathrm{A}] = -k_1^{/}[A]$$

$$[A] = [A]_0 e^{-k_1^{/}t} = [A]_0 e^{-k_2[B]t}$$

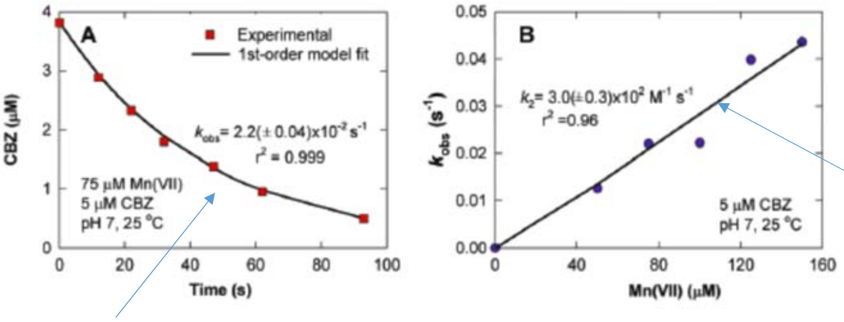
$k_1^{/}$ (s^{-1})

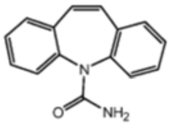
$$A + B \xrightarrow{k_2} C$$



Experimental determination of 2^{nd}-order rate constants.

- Experimentally, we measure k_1' values for degradation of "A" in the presence of a range of [B] values where [B] >> [A]
    - E.g., oxidation of the anticonvulsant drug carbamazepine by permanganate, Mn(VII):





carbamazepine (CBZ)

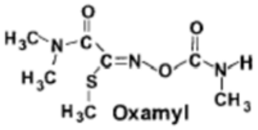
$k_1' = k_2[\mathrm{Mn(VII)}]$

A) Measured CBZ decay in batch reaction follows pseudo-1^{st}-order rate law when [Mn(VII)] >> [CBZ]

Hu et al. (2009) Environ. Sci. Technol. 43, 509

Problem 3: In the earlier example with oxamyl, the kinetic rate law was actually a pseudo-first-order rate law. The actual reaction is more accurately described by a second-order rate law

$$\frac{d[\text{Oxamyl}]}{dt} = -k_2[\text{Oxamyl}][\text{OH}^-]$$



Where $k_2 = 3\text{x}10^4\ \text{M}^{-1}\ \text{h}^{-1}$ and $[\text{OH}^-] = 10^{-7}$ M at pH 7.

So, $k_1' = k_2[\text{OH}^-] = (3\text{x}10^4\ \text{M}^{-1}\ \text{h}^{-1})(10^{-7}\ \text{M}) = 3\text{x}10^{-3}\ \text{h}^{-1}$ (takes 760 hrs to degrade to MCL)

It also follows that we should be able to estimate the time needed for oxamyl to degrade from 2 mg/L to the MCL value of 0.2 mg/L at different pH conditions.

At pH 8:

At pH 6:

Kinetics

Svante Arrhenius
(1859-1927)

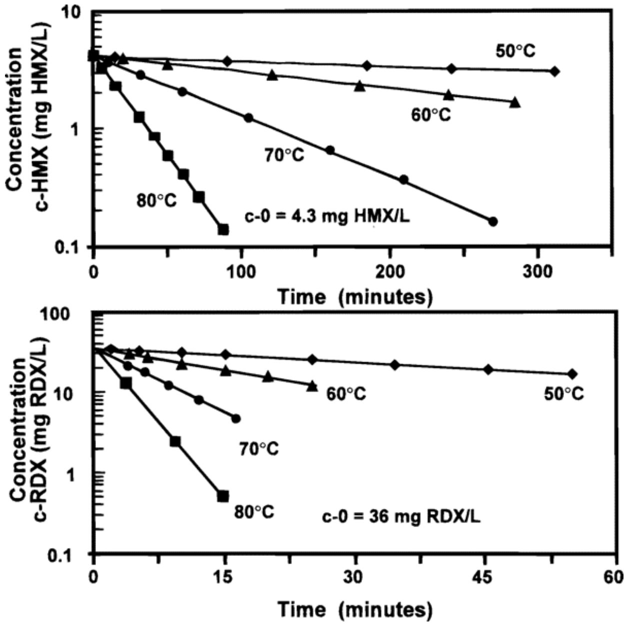
- Effect of temperature
  - Arrhenius
    - ion dissociation and activity coefficient (1884)
    - first mention of greenhouse gas theory (1897)
    - effect of temperature on reaction kinetics

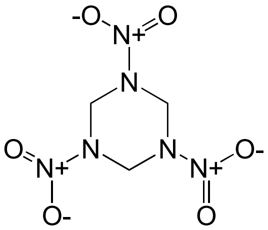
$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

$$\ln\frac{k_{T2}}{k_{T1}} = \frac{E_a(T_2 - T_1)}{RT_1T_2}$$

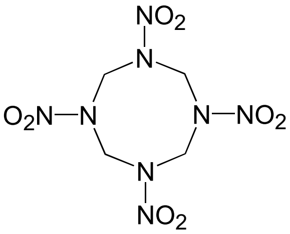
Kinetics

- E_a determined experimentally
  - RDX, HMX
    (high explosives)
  - alkaline hydrolysis
    (Heilmann et al., 1996, *ES&T* 30, 1485)





RDX



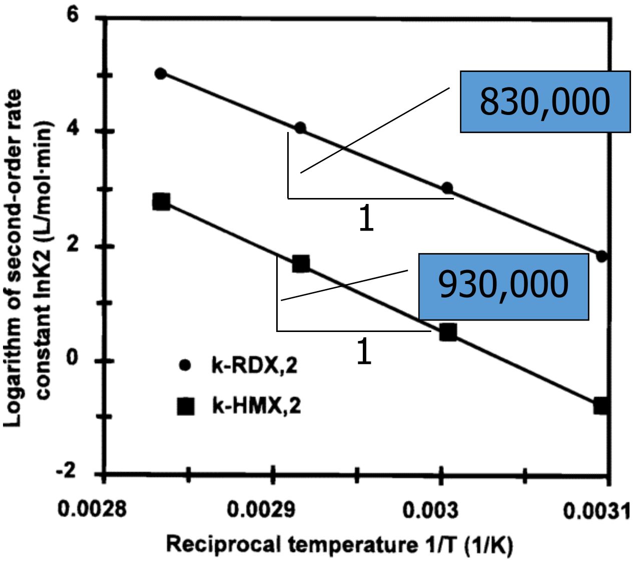
HMX

Kinetics

- E_a determined experimentally

$$\ln k = -\left(\frac{E_a}{RT}\right) + \ln A$$

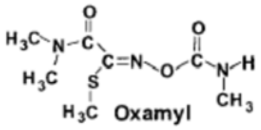
  - plot ln*k* vs 1/*T*
  - slope is $-E_a/R$
  - RDX: 100 kJ mol^{-1}
  - HMX: 112 kJ mol^{-1}

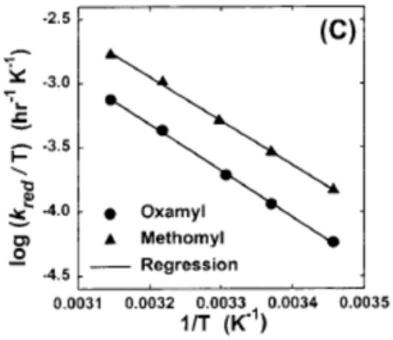


Problem 4: The E_a value for oxamyl degradation by hydrolysis is 69 kJ/mol, and the k_2 value at 25°C is $3\text{x}10^4$ M^{-1} h^{-1}. What is the expected half life at 5°C and pH 7.5?

$$\frac{d[\text{Oxamyl}]}{dt} = -k_2[\text{Oxamyl}][\text{OH}^-]$$

$$\ln k_{T2} = \ln k_{T1} + \frac{E_a(T_2 - T_1)}{RT_1T_2}$$





Wrap-up

- Rate law models determined experimentally
- Diagnostic plots (if linear)
  - 1st order: ln[A] vs. time
  - 2nd-order: ln([A]/[B]) vs. time
  - 0th-order: [A] vs. time
- Apply integrated rate laws to solve for time dependence of reactants and products
- Effect of Temperature – Arrhenius Equation