Process Kinetics

Lab Lecture the week of Oct 19

Lab held in Marston 10 the week of Oct 26

Objective

- Develop a kinetic rate equation for the destruction of Naproxen with aqueous chlorine
- Use the rate equation to assess relative costs of a water and wastewater treatment to inform process design
  - Naproxen: a synthetic compound used as an anti-inflammatory drug, especially in the treatment of headache and arthritis

What is Kinetics?

- The study of :

1. the *speed* with which a chemical reaction occurs: ***the rate at which the concentrations of reactants and products change***

and,

2. the *factors* that affect this speed
   - Concentration
   - Temperature
   - Phase (solid, liquid, or gas)
   - Surface area
   - Solvent
   - Presence/absence of a catalyst

Reaction Rate (r)

- The rate of formation or consumption of a compound (r)

$$aA + bB \rightarrow pP$$

Rate of destruction of A

Rate of destruction of B

Rate of formation of P

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt}$$

$$-r_A = -r_B = r_P$$

The reaction ***order*** is the sum of the power of exponents

$$r = d[A]/dt = - k[A]^a[B]^b$$

k - reaction rate constant; dependent on temperature and pressure

Summary of Reaction Kinetics

Order	Reaction	Rate Equation	Integrated Form ($A=A_0$ at t=0)	Half-Life (t for $[A]=0.5 A_0$]
0	$A \rightarrow B$	$d[A]/dt = -k$	$[A]=A_0 - kt$	$A_0/2k$
1	$A \rightarrow B$	$d[A]/dt= -k[A]$	$[A]=A_0 e^{-kt}$	0.693/k
2	$A+A \rightarrow B$	$d[A]/dt = -k[A]^2$	$1/[A]=1/A_0 + kt$	$1/kA_0$
	$A+B \rightarrow P$	$d[A]/dt = -k[A][B]$	$\ln([B]/[A])= \ln(B_0/A_0) + (B_0-A_0)kt$ (for $A_0 \neq B_0$, $[B]=B_0$ at t=0)	

From Benjamin and Lawler (2012)

Determining Order of Reaction by Method Integration

Plotting Procedure to Determine Order of Reaction by Method of Integration

Order	Rate Equation	Integrated Equation	Linear Plot	Slope
0	$d[A]/dt = -k$	$[A] - [A]_0 = -kt$	$[A]$ vs. t	$-k$
1	$d[A]/dt = -k[A]$	$\ln[A]/[A]_0 = -kt$	$\ln[A]$ vs. t	$-k$
2	$d[A]/dt = -k[A]^2$	$1/[A] - 1/[A]_0 = kt$	$1/[A]$ vs. t	k

Source: Henry and Heinke, 1989. Reprinted with permission.

Chlorine as a Disinfectant

- Used in both water treatment and wastewater treatment to disinfect and deactivate germs
- Very strong oxidant and will inactivate microorganisms and also react with other water constituents
- Three forms of chlorine in water treatment
  - Free: chlorine composed of dissolved hypochlorite ions, hypochlorous acid, and chlorine gas
  - Combined: chlorine in water combined with ammonia to form chloramines
  - Total: sum of free and combined chlorine
- Efficacy:
  - $HOCl > OCl^{-} >$ inorganic chloramines > organic chloramines

Residual Chlorine

- The amount of chlorine that remains in the water after a certain period of contact time

http://controlsystem-design.com/bnr-oxygen-control/wastewater-disinfection-control/

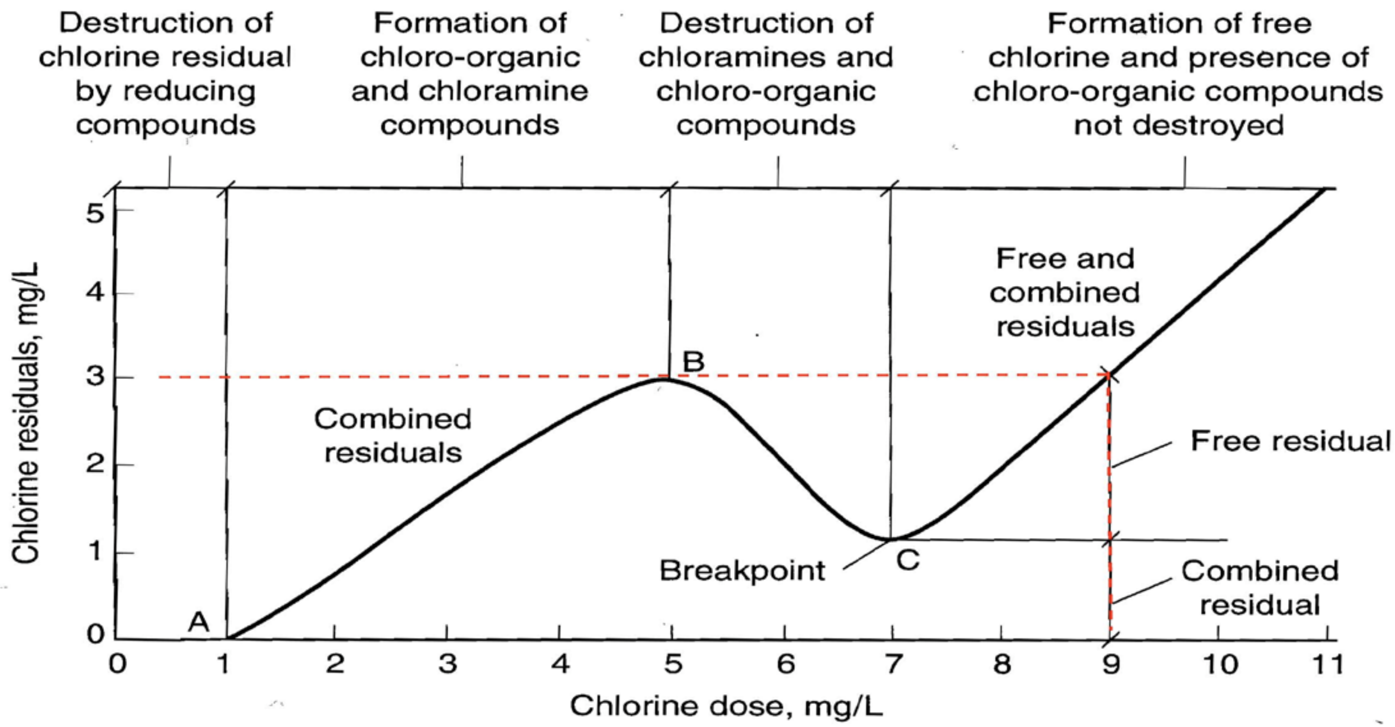
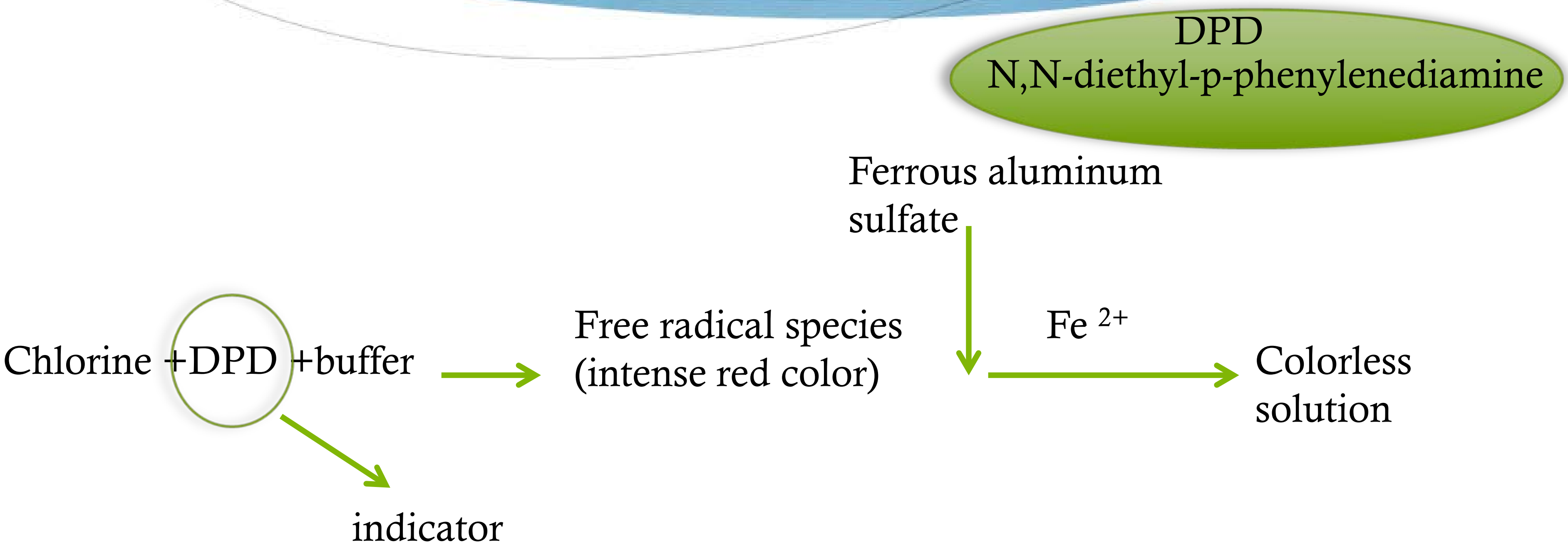


Figure 1: Breakpoint chlorination curve

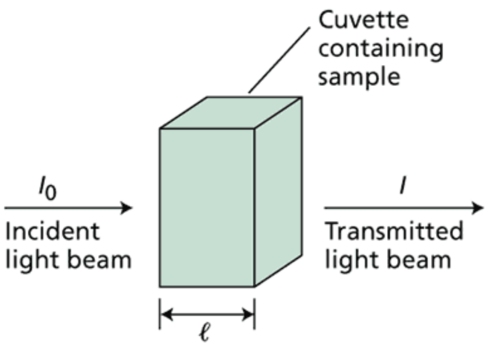
To measure residual chlorine concentration



- No. of mLs titrant used = chlorine residual in mg/L Cl_2
- (back calculate to original sample conc. using dilution factor).

To measure UV absorbance

- A UV-Vis Spectrophotometer will be used
- Basic theory of molecular absorption spectroscopy is basied on the measurement of the absorbance A (or transmittance T) of solution contained in a transparent cell with a path length l (Skoog et al., 2007).



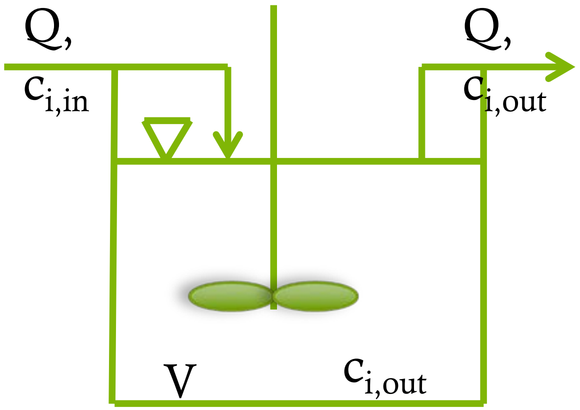
- Beer's Law: The concentration of the absorbing analyte is linearly related to tl

$$A = -\log T = \log \frac{I_0}{I} = \varepsilon l c$$

I_0 is radiant power in watts incident on sample; I is radiant power transmitted by sample; ε is molar absorptivity ($M^{-1}cm^{-1}$); l is length over which attenuation occurs (usually 1 cm, which is what we'll be using); c is concentration in specified units (usually in M)

Useful Information CFSTR

- Continuous flow stirred tank reactor (CFSTR) at steady state:



$$V\frac{dc_{i,out}}{dt} = Q(c_{i,in} - c_{i,out}) + Vr$$

$$0 = Q(c_{in} - c_{out}) + Vr_i$$

$$\tau = V / Q$$

$$\tau_{CFSTR} = -\frac{C_{in} - C_{out}}{r_{c_{out}}}$$

Useful Information CFSTR

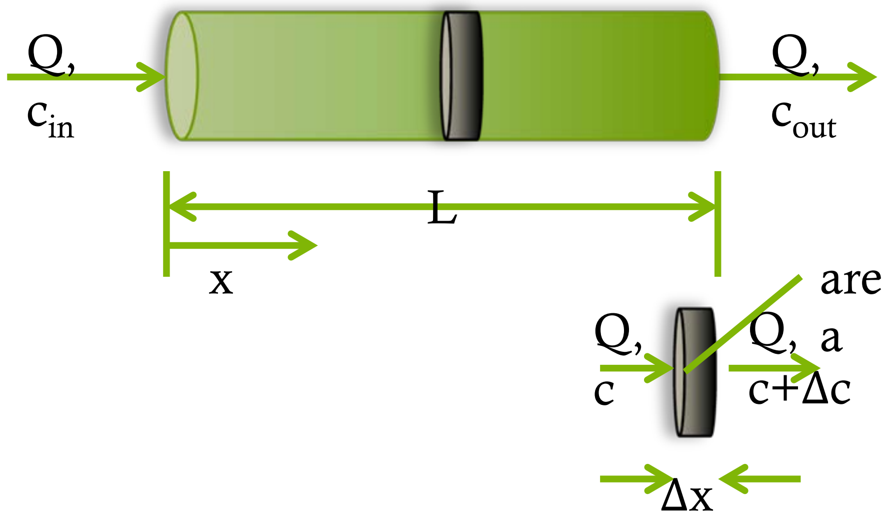
Reaction order, n ($r=-k_n c^n$)	C_{out}	C_{out}/C_{in}	τ_{PFR}
0	$c_{in}-k_0\tau$	$1-(k_0\tau/c_{in})$	$1/k_0 * (c_{in}/c_{out})$
1	$c_{in}\exp(-k_1\tau)$	$\exp(-k_1\tau)$	$1/k_1 * \ln(c_{in}/c_{out})$
2	$c_{in}/(1+k_2\tau c_{in})$	$1/(1+k_2\tau c_{in})$	$1/k_2 c_{in} * ((c_{in}/c_{out})-1)$

From Benjamin and Lawler (2012)

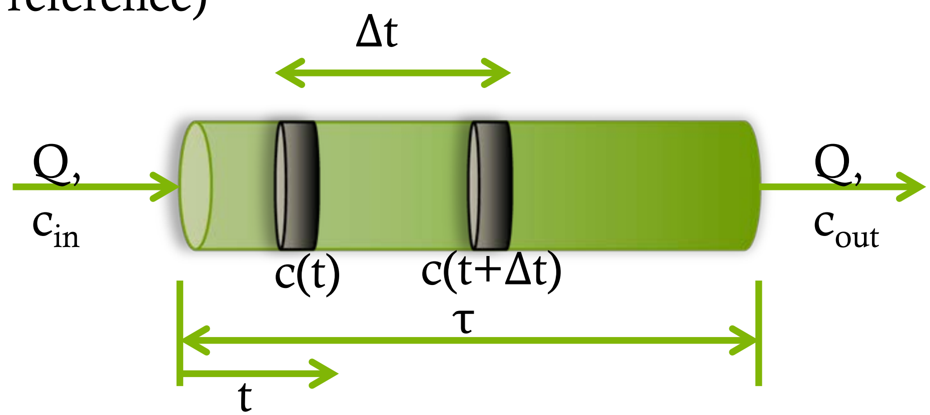
Useful Information
PFR

Plug-flow reactor (PFR):

Eulerian View (fixed frame of reference)



Langrangian View (moving frame of reference)



Useful information PFR

Reaction order	C_{out}	C_{out}/C_{in}	τ_{PFR}
0	$c_{in}-k_0\tau$	$1-(k_0\tau/c_{in})$	$C_{out}/k_0 * ((c_{in}/c_{out})-1)$
1	$c_{in}/(1+k_1\tau)$	$1/(1+k_1\tau)$	$1/k_1 * ((c_{in}/c_{out})-1)$
2		$1/(1+k_2\tau c_{out})$	$1/k_2c_{out} * ((c_{in}/c_{out})-1)$

From Benjamin and Lawler (2012)

Comparison of CFSTRs and PFRs

- For first and second order reactions, more detention time is required in a CFSTR than a PFR to accomplish the same amount of removal.
- For a zero-order reaction, the two systems perform identically
- Why use CFSTRs?
  - Water and wastewater treatment equalization basins
  - Mixing of chemicals
  - Less dead space and short circuiting