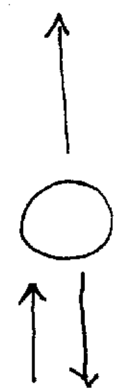
11/17/99

Sedimentation

Gravity (or centrifugal) as driving force

displaced solvent is also pulled by gravity



Driving Force Net = [Gravity] − [Bouyancy]

$$= mg - (m \bar{v}_2 \rho) g$$

$$= mg(1 - \bar{v}_2 \rho)$$

Terminal velocity is reached when fu = Driving Force

$$mg(1 - \bar{v}_2\rho) = f u_t$$

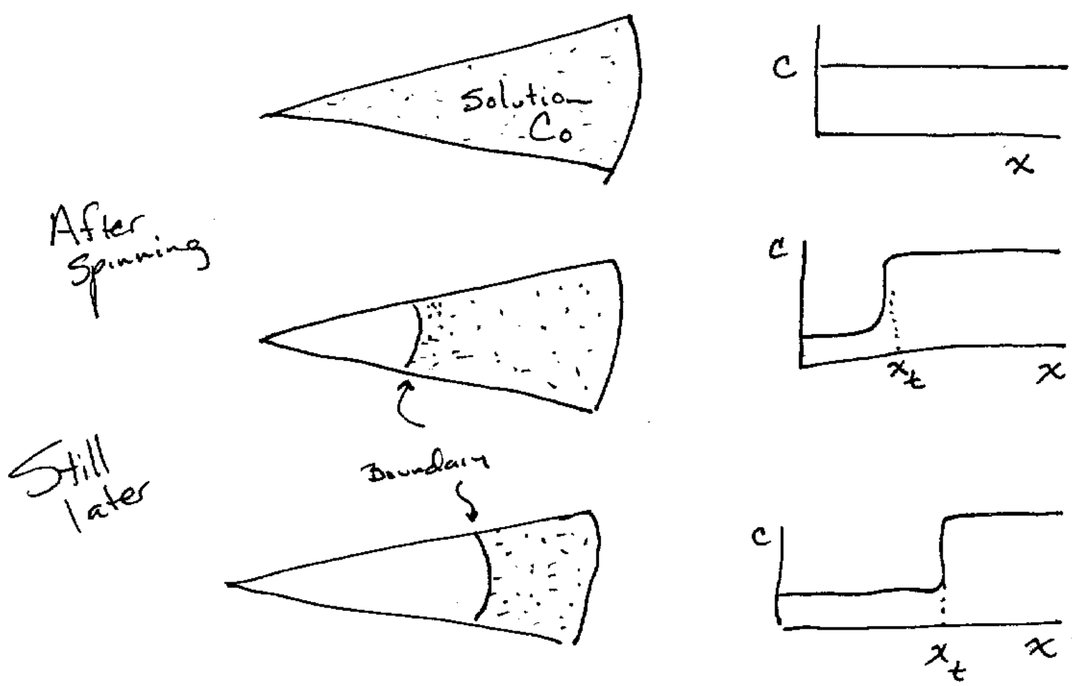
$$U_t = \frac{m(1 - \bar{v}_2\rho) g}{f}$$

Now replace gravitational acceleration g
by centrifugal acceleration $\omega^2 x$

$$U_t = \frac{m(1-\bar{v}_2\rho)}{f}\,\omega^2 x$$

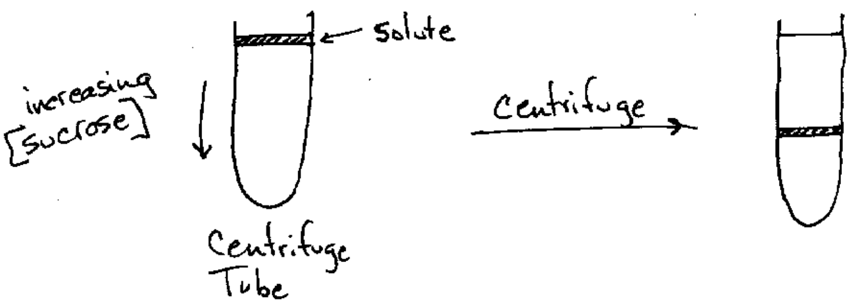
$$\underbrace{\frac{U_t}{\omega^2 x}}_{\text{experimental stuff}} = \text{sedimentation coefficient} = s = \underbrace{\frac{m(1-\bar{v}_2\rho)}{f}}_{\text{fundamental properties of solute and solvent}}$$

⟹ Boundary Sedimentation



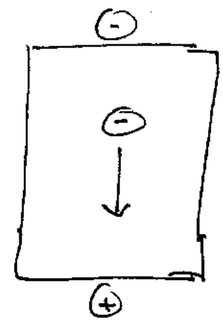
$$s = \frac{U_t}{\omega^2 x} = \frac{\left(\frac{\partial x_{1/2}}{\partial t}\right)}{\omega^2 x_{1/2}} = \frac{1}{\omega^2}\frac{\partial \ln x_{1/2}}{\partial t} = \frac{2.303}{\omega^2}\frac{\partial \log x_{1/2}}{\partial t}$$

⇒ Zone Sedimentation



No details here

Electrophoretic Mobility



Force is electrical

$$\text{Mobility} = \mu = \frac{\overset{\text{velocity}}{u}}{\underset{\text{electric field}}{E}} = \frac{ZeE}{f}$$

(Typo on page 313
Mobility = u/E (not μ/E))

Empirically $\quad \log M = a - bx$

M: protein molecular weight

a, b: Empirical parameters from standards

x: distance migrated

Requirements for reactivity between A and B?

1) Collision – can't react if far apart

2) Have sufficient energy to overcome barriers
   a) initial breaking of bonds
   b) anything subsequent...

So. Look at how conditions might influence:

1) Concentration – increasing concentration increases number of collisions

we saw before for a pure gas that

$$Z_1 = 2\sqrt{\pi}\left(\frac{N}{V}\right)^2\sigma^2\left(\frac{RT}{M}\right)^2$$

↑ Concentration

So for a reaction $A + A \rightarrow P$
we'd predict Rate $\propto C^2$ (It is!) (Generally...)

2) Temperature a) also increases collision frequency

b) BUT also increases the energy associated with each collision. This gets to the must "have sufficient energy to overcome barriers."

Would that it were so simple!

The "sufficient energy to break barriers" is complex.

Nevertheless, we must understand the kinetics of a reaction to fully understand mechanism.

IMPORTANT CONCEPTS:

1) Collision – we just saw.

2) Transition State (and reactants ground state and products ground state)

3) Rate-Determining Step

We'll come back to this, but first some practical concepts.

$$\text{Velocity} = v = \frac{\partial c}{\partial t} = \text{rate (velocity) of a reaction}$$

$$\text{Rate Law} \Rightarrow v = f(c)$$

function f is the Rate Law

understanding this is key to understanding mechanism

(Trick) Question: For a reaction: $A + B \longrightarrow C$
What is the rate law?

Answer: We can't know. (without more information)

IMPORTANT CONCEPT #1

$A + B \rightarrow C$ only tells us stoichiometry

Reactants (A,B) → decrease with time
Products (C) → increase with time

Intermediates (?) → increase, then decrease

As in:

Intermediates

$A + B \rightarrow Q \rightarrow X \rightarrow C$

Things which don't change concentration:

Catalysts (enzymes, inhibitors, non-reactant factors)
Intermediates at steady state (definition of steady state)
Solvents
Species coupled to infinite pools (practically).

Important Concept #2

ORDER OF A REACTION

If the rate law is: $v = \frac{\partial C}{\partial t} = kA^2B$

then the order of the reaction w/ respect to A is 2
" " " " " B is 1

ie. the exponent of X in the rate law

N.B. The stoichiometry of a reaction tells us nothing necessarily about the rate law.

Perhaps $A + B \rightarrow C$

goes via $A + A + B \xrightarrow{\text{slow}} A \cdot A \cdot B \xrightarrow{\text{fast}} A \cdot C \xrightarrow{\text{fast}} A + C$

in this case, one molecule of A is a <u>reactant</u> (consumed)

but another molecule of A is a <u>catalyst</u> (comes out unchanged)

$A + B \xrightarrow{\text{slow}} AB \xrightarrow[\text{fast}]{A} A \cdot A \cdot B \xrightarrow[\text{fast}]{} A \cdot C \xrightarrow[\text{fast}]{} A + C$

might show $\frac{\partial c}{\partial t} = v = k A B$

While

$A + B \xrightarrow{\text{slow}} AB \xrightarrow[\text{slow}]{A} A \cdot A \cdot B \xrightarrow[\text{fast}]{} A \cdot C \xrightarrow[\text{fast}]{} A + C$

would/could show something between the two

$\frac{\partial c}{\partial t} = v = k A^{1.5} B$ (Yikes!)

<u>ie.</u> it's <u>messy</u>.