Sedimentation → Driving $F$ → Frictional $F$

Gravity (or centrifugal) as driving force

Displaced solvent is also pulled by gravity

[Bouyancy] $m \bar{v}_2 \rho g$ → $mg$ [Gravity pulls down]

Driving Force Net = [Gravity] - [Bouyancy]

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

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

Terminal velocity is reached when $fu = \text{Driving Force}$

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

$U_t = \frac{m (1 - \bar{v}_2 \rho) g}{f}$
Now replace gravitational acceleration $g$ by centrifugal acceleration $\omega^2 x$

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

$$\frac{U_t}{\omega^2 x} = \frac{\text{Sedimentation Coefficient}}{\text{experimental stuff}} = S = \frac{m(1-\bar{\rho}_2 \rho)}{f}$$

Fundamental properties of solute and solvent

$\Rightarrow$ Boundary Sedimentation

After spinning

Still later

$$S = \frac{U_t}{\omega^2 x} = \frac{(\frac{\partial x}{\partial t})}{\omega^2 x^{1/2}} = \frac{1}{\omega^2} \frac{\partial \ln x^{1/2}}{\partial t} = \frac{2.303}{\omega^2} \frac{\partial \log x^{1/2}}{\partial t}$$
Zone Sedimentation

Electrophoretic Mobility

\[ \text{Mobility} = \mu = \frac{U}{E} = \frac{ZeE}{f} \]

(Typo on page 313)

Mobility = \( \frac{U}{E} \) (not \( \frac{U}{E} \))

Empirically

\[ \log M = a - bx \]

Protein molecular weight

Empirical parameters from standards

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

\[ z = \frac{8 \pi r^2}{3} \left( \frac{N}{V} \right)^2 \left( \frac{RT}{M} \right)^2 \]

\[ \text{Concentration} \]

So for a reaction \( A + A \to P \)

We'd predict Rate \( \propto C^2 \) \( \text{It is!} \) \( \text{(Generally...)} \)

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.

\[ \text{Velocity} = \dot{v} = \frac{dc}{dt} = \text{rate (velocity) of a reaction} \]

Rate Law \[ \Rightarrow \dot{v} = f(c) \]

function \( f \) is the Rate Law

understanding this is key to understanding mechanism

(Trick) Question: For a reaction: \( A + B \rightarrow C \)

What is the rate law?

Answer: We can't know. (without more information)
A + B \rightarrow C \quad \text{only tells us stoichiometry}

Reactants (A, B) \rightarrow \text{decrease with time}
Products (C) \rightarrow \text{increase with time}

Intermediates (?) \rightarrow \text{increase, then decrease}

As in: \quad \text{Intermediates}
\quad A \rightarrow 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).

ORDER OF A REACTION

If the rate law is: \quad \frac{\text{d}c}{\text{d}t} = kA^2B

then the order of the reaction with respect to A is 2
B is 1

ie. the exponent of X in the rate law

\text{N.B.} \quad \text{The stoichiometry of a reaction tells us nothing necessarily about the rate law.}
Perhaps \[ A + B \rightarrow C \]

goes via \[ \begin{align*}
A + A + B & \rightarrow A \cdot A \cdot B \\
& \rightarrow A \cdot C \\
& \rightarrow A + C
\end{align*} \]

in this case, one molecule of \( A \) is a \underline{reactant} (consumed)

but another molecule of \( A \) is a \underline{catalyst} (comes out unchanged)

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

might show \[ \frac{\Delta c}{\Delta t} = \gamma = k AB \]

While

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

would could show something between the two

\[ \frac{\Delta c}{\Delta t} = \gamma = k A^{1.5} B \quad (\text{yikes!}) \]

ie. it's messy.