Experiment #2

Primary Salt Effects on the Kinetics of Ionic Reactions
Introduction

• Oppositely charged reactants experience an attractive force that pulls them together whereas like charged reactants experience a repulsive force that tends to keep the reactants apart.

• These electrostatic forces have their full strength in the gas phase, but the forces are decreased when the ions are in a solution, “charge screening” effects.

• This experiment investigates how the presence of other ions can affect the rates (and equilibrium) of chemical reactions between ions, i.e., “non-common ion effect”.
Primary Ion Effect

\[ AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \]

- When some KNO\textsubscript{3} is added to the silver chloride solution, the KNO\textsubscript{3} dissolves as K\textsuperscript{+}(aq) and NO\textsubscript{3}\textsuperscript{−}(aq) ions. There will tend to be more NO\textsubscript{3}\textsuperscript{−} than K\textsuperscript{+} that will find themselves around Ag\textsuperscript{+}(aq) ions, and more K\textsuperscript{+} than NO\textsubscript{3}\textsuperscript{−} around Cl\textsuperscript{−}(aq).
- The presence of non-common ions will tend to increase the solubility of silver chloride because they decrease or shield the electrostatic forces between the silver and chloride ions.
Effects on Chemical Kinetics

- Because of primary ion effect, the rate of a reaction between oppositely charged ions will tend to decrease because of the shielding effect of additional ions, while the rate for a reaction involving like charged ions will increase with increasing ion concentration.
- The effects of the additional ions in aqueous solution are demonstrated in the activity coefficient of the reacting species.
- The activity coefficient depends on the ionic strength of a solution and reflects how much the behavior of a substance deviates from ideal behavior.
Transition State Theory

- Rate of chemical reaction, $A + B \rightarrow \text{products}$

$$k = \frac{k_B T}{h} K \frac{\gamma_A \gamma_B}{\gamma_{M^*} \gamma_{M^*}} = k_0 \frac{\gamma_A \gamma_B}{\gamma_{M^*} \gamma_{M^*}}$$

Debye-Huckel theory (very dilute solutions)

$$\log \gamma_i = -z_i^2 A \sqrt{\beta}$$

$$\log k = \log k_0 - z_A^2 A \sqrt{\beta} - z_B^2 A \sqrt{\beta} + z_{M^*}^2 A \sqrt{\beta}$$

aqeous solutions: $A = 0.509 @ 298K$
Brønsted Relation

\[ \log \frac{k}{k_0} = 1.02 z_A z_B \beta^{1/2} \]

where \( \beta = \frac{1}{2} \sum c_i z_i^2 \) is the ionic strength.

- The rate constant should increase with increasing ionic strength, \( \beta \), when the reacting ions have the same charge and should decrease with increasing ionic strength when the reacting ions are oppositely charged.

- This effect is called the primary salt effect.
Chemical Reaction

- $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$  Rate-determining step
- $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$  Fast reaction

$$- \frac{d}{dt} \left[ \text{S}_2\text{O}_8^{2-} \right] = k_{\text{app}} \left[ \text{S}_2\text{O}_8^{2-} \right] \quad \text{and} \quad k_{\text{app}} = k[\text{I}^-]$$

$$- \frac{d}{dt} \left[ \text{S}_2\text{O}_8^{2-} \right] = \frac{\Delta x}{\Delta t}$$

where $\Delta x$ is the number of moles of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ion added to the solution, and $\Delta t$ is the time elapsed from the moment of mixing of the persulfate ($\text{S}_2\text{O}_8^{2-}$) with the reagents until the blue color appears.
Primary Salt Effect

- Varying the ionic strength of the medium through the addition of neutral electrolyte (KNO₃), one can test whether the Brønsted relationship is obeyed.

### Table 1. Volume of Reagents Added (in Milliliters)

<table>
<thead>
<tr>
<th>Flask No.</th>
<th>10⁻¹ M KI</th>
<th>10⁻³ M Na₂S₂O₅</th>
<th>1 M KNO₃</th>
<th>Solvent</th>
<th>Starch</th>
<th>10⁻² M K₂S₂O₈</th>
<th>Δt</th>
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Rate = Δx/Δt
### Experimental Data

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<tr>
<th>Flask</th>
<th>Rate</th>
<th>$\beta^{\frac{1}{2}}$</th>
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**Ionic strength includes all ionic species**
Starch Iodine Test

Starch - Coiled Structure - due to alpha acetal

Starch - Iodine Complex

\[ I_2 + I^- \rightarrow I_3^- \]

Iodine slides into starch coil to give a blue-black color

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