Reactions in Non-Ideal Solutions - The Effect of Ionic Strength on the Rate of Reactions Between Ions in Aqueous Solution (the Kinetic Salt Effect)

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Experiment Overview

In chemistry, many experiments rely on a comparison of experimental results to theoretical models. For the most part, such comparisons are valid and reliable. In many cases, however, a theoretical expression may only be applicable under certain experimental conditions. For example, an ion selective electrode may only act in accordance with the Nernst Equation under a specified pH or temperature range. It is therefore important for students to be aware of potential limitations that may exist in order to reliably interpret experimental results using theoretical models.

In the teaching laboratory, exercises are normally pre-tested to ensure that experimental conditions yield results that consistently comply with theoretical expectations. Students may therefore become complacent when attempting to explain 'errant' results, automatically attributing them to 'student error' without considering alternative possibilities.

In this experiment, results are compared to the theoretical predictions of the Kinetic Salt Effect (which incorporates the Debye-Hückel Limiting Law). However, the experimental conditions have been designed to be non-compliant with specific limitations of the theoretical model. The experimental results adhere to general theoretical expectations, and the low degree of scatter in plotted data indicates that the experiment was carried out successfully, with minimal 'student' or 'experimental' error. Nonetheless, the results do not match the theoretical prediction of the Kinetic Salt Effect. Students are prompted to question the applicability of the theoretical model to their results. Their calculations reveal all solutions to have an ionic strength exceeding the specified limits of the Debye-Hückel Limiting Law. This determination triggers students to critically assess the applicability of theory to experiment when analysing data.

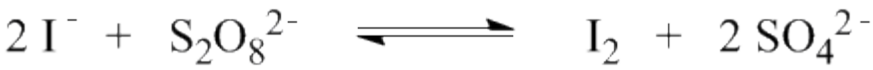
Further points of consideration that make this experiment an effective learning tool include:

- the use of volumetric glassware
- indirectly monitoring the progress of a reaction
- catalytic effects on the rate of a reaction
- performing calculations fundamentally applicable to chemistry
- applying graphical analysis to experimental data
- the reaction studied is described by Activated Complex Theory (which is introduced in the Background Theory for the experiment).

Aims and Objectives

In this experiment the Kinetic Salt Effect (the impact that increasing ionic strength has on the rate of a reaction in ionic solution) is explored. Students compare their findings to theoretical predictions. While being a simple experiment it offers several points of consideration for the student, making it an effective learning tool:

- Indirect measurements of chemical species. The reaction product (iodine) is difficult to measure directly, thus it is simpler and more accurate to monitor its production indirectly.
- The effect that altering a reaction mixture can have on the rate of a reaction. The reaction studied in the experiment is:



The observed effect (reaction rate increases with increasing ionic strength) can be explained simply as the positive ion of the added electrolyte (Mg^{2+}) draws the two negatively charged reactants closer, increasing the chance of a successful reaction. Students gain confidence when they are able to explain (perhaps with some prompting) an observation in a way that is clearly easy to understand. (Note that this can be expanded upon, however, if lecture material covers more extensive properties of ionic solutions including the Debye-Hückel theory of ionic solutions and the affect of 'ionic atmosphere' on ion reactivities.)

- While the equation(s) used are 'simple', they do require quite a bit of number crunching, which leads to satisfaction when completed successfully.
- Recognising a linear form of an equation and subsequent plotting of relevant data is always beneficial in Chemistry!
- Comparing experimental results with theoretical proposals triggers students to critically assess the applicability of theory to experiment. In this experiment, the theory is not obeyed (however limiting slopes may show that the theory is approached). Calculations show clearly that one assumption connected to the theory is not met (ionic strength exceeds the limit on which the theory is based). Students can therefore realise that failure to comply with theoretical expectations is not always simply due to 'student error', and it is therefore imperative that applicability of theory to each experimental protocol is also assessed.
- Activated Complex Theory describes the reaction taking place, and is introduced in the Background Theory for the experiment.

Level of Experiment

Second year undergraduate

Keyword Descriptions of the Experiment

Domain
physical chemistry

Specific Descriptors
ionic strength, kinetic salt effect, Debye-Huckel theory of ionic solutions, activated complex theory

Course Context

This experiment has a direct bearing on kinetics (with respect to reaction rates, catalytic effects etc.). It also deals with ideal and non-ideal solutions, ionic strength, activity coefficients, Debye-Hückel theory related to ion-ion reactions, and activated complex theory (ACT). Knowledge in these areas would naturally assist students, however the concepts are not too complicated and are covered in the laboratory notes.

Prerequisite Knowledge and Skills

Experimental skills required are the ability to use volumetric glassware – and simply being able to work a stopwatch.

Time Required to Complete

Prior to Lab: 30 min - 1 h (reading)
In Laboratory: 2 - 3 h
After Laboratory: 2 - 3 h (plotting data, analysing results, calculations, report writing)

Submission Details

While the origin of this experiment is unknown by the submitter, it has been adapted from past Physical Chemistry II laboratory course experiments implemented in the Department of Chemistry at The University of Adelaide.