Reactions in non-ideal solution - The effect of ionic strength on the rate of reactions between ions in aqueous solution (the kinetic salt effect): An APCELL Experiment *

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Introduction
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).

Educational Template

Section 1 - Summary of the Experiment

1.1 Experiment Title
Reactions in Non-Ideal Solution - The Effect of Ionic Strength on the Rate of Reactions between Ions in Aqueous Solution (The Kinetic Salt Effect)

1.2 Description of the Experiment
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:

$$2I^- + S_2O_8^{2-} \rightleftharpoons I_2 + 2SO_4^{2-}$$

  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

*The complete documentation for this experiment is freely available on the APCELL web site [www.apcell.org]. It includes the educational template, a set of student notes, demonstrator notes and technical notes to allow ready implementation into a new laboratory.

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.

1.3 Course Context and Students' Required Knowledge and Skills

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.

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

1.4 Time Required to Complete

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

1.5 Acknowledgments

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.

Section 2 – Educational Analysis

Learning Outcomes *What will students learn?*	**Process** *How will students learn it?*	**Assessment** *How will staff know students have learnt it?* *How will students know they have learnt it?*

Theoretical and Conceptual Knowledge

Backing up, clarifying or extending knowledge gained from lectures, tutorials, and self-study in the areas of: a) Ideal / non-ideal solutions b) The activity coefficient c) Ionic Strength, Debye-Hückel limiting law, and Kinetic Salt Effect d) Activated Complex Theory (ACT) e) Effects on reaction rates ('catalysis')	a-d) Students compare the results of their experiment to theoretical expectations based on a combination of these points, which are described in the Student Notes. e) Students see directly the catalytic effect the increase in ionic strength has on the reaction rate of their reaction mixtures.	a-d) Students are required to write a report on their experiment, following guidelines provided in general laboratory notes. The Introduction section and Discussion section of their report is usually a solid indicator on whether or not a student has grasped the relevant concepts, as gauged not only by the accuracy of their report but also by its originality (e.g. explaining concepts 'in their own words'). e) If this is understood, students will be able to explain why their reaction rate increased on addition of electrolyte.

Scientific and Practical Skills

Volumetric techniques	Students make a series of solutions that require the use of volumetric glassware.	By observing their experimentally derived plot. While it should not be linear as theory predicts, it should still follow a smooth trend which would confirm that good volumetric technique was achieved.

Generic Skills

Ability to collate, correlate, display, analyse and report observations. Ability to present reports in appropriate formats.	Students record their experimental results, perform calculations on their results and construct relevant graphs. Students then construct a written report on conclusion of their experiment, following (if desired) clear guidelines presented in their manual.	Assessment of their written report is based not only on content, but also on appropriate presentation adhering to standard form (e.g. abstract, aim, introduction, experimental, results, discussion, conclusion, references).
Ability to consider limitations of theories when they are applied to practical applications.	Students discover that while their results follow the general expectations, they do not obey an expected trend based on theoretical predictions. 'Experimental error' cannot account for the deviation from theory as the results are neither erratically scattered nor biased. Students are therefore prompted to question the applicability of the theoretical prediction to their results: In this case, their calculations reveal all solutions to have an ionic strength > 0.01, yet the theory is based on an assumption of ionic strength < 0.01.	By recognising non-compliance to the theoretical prediction and explaining why this occurred. Students who do not accomplish this learning objective may attempt to 'force' a straight line through their data, 'fudge' a few data points to ensure linearity, or simply state that "the theory is obeyed as a straight line is observed… within experimental error anyway…"
Manipulation and presentation of data (plotting, spreadsheeting, etc)	Calculations of molarity followed by calculations of ionic strength for each reaction mixture is required. In our laboratory, students are able to perform these calculations how they wish. The calculations are complex enough, however, that a spreadsheet would be advantageous. Students are required to plot their graph(s) using computer software.	Correct manipulation of data can be checked by referring to 'model answers' provided to demonstrators. A predictable plot (slightly curved) is also indicative of successful data manipulation (as well as collection).
Problem solving: ability to apply problem solving in familiar and unfamiliar situations, and to display the capability of rigorous and independent thinking.	Students observe trends in their results that are expected (reaction rate increases with ionic strength), yet the results do not match the prediction of linearity given in the theory. These observations are easily explained after some thought by the student (with a little prompting by questions posed in the laboratory write-up). This encourages students to approach experimentation laterally, and to explore more than 'experimental error' when attempting to explain unexpected results.	Explanations of the observed results in the students written reports, as well as through oral communication/ assessment with the demonstrator.

Working with others: one-to-one and in teams, understanding and responding to the demands of the task and working effectively to achieve a shared goal, coping with set backs.	The experiment is typically undertaken in pairs, with sharing and / or division of tasks being established by the students themselves. The observations of predictable trends in their results, followed by the realisation that their results do not match theoretical predictions can also encourage teamwork as students work together to discover why. On occasion, students will question each other's technique before questioning limitations that may be applicable to the theory. Teamwork can be enhanced when the students determine that neither they nor their partner have erred.	Teamwork is noticed as being effective during the course of the experiment, by observing the students setting up the equipment, running the experiment and analysing and interpreting data, as well as addressing questions posed in the manual. Poor teamwork can sometimes be noticed if a student does not have all relevant measurements in his/her written report after the laboratory session. Oral assessment at the conclusion of the experiment is usually performed by the demonstrator on each group rather than individual students. During this time, the demonstrator discusses points of the experiment with each student in the group.
Life-Long Learning: the capacity for and commitment to life-long learning.	In my opinion the ability to question before accepting is essential to life-long learning. This experiment encourages this approach, as the results the students obtain do not obey a theoretical relationship introduced in their Student Notes. On the other hand, the results do support the general theoretical expectations, and appear to be reliable as they follow a definite trend with very little scatter. Considering that both the theory and the experimentation are sound, students must therefore question what they have been told in order to understand the 'discrepancy' they see.	This will be indicated by students showing (through verbal communication as well as written reports) that they recognise that the experimental results do not match the theory yet both are sound. By successfully explaining the 'discrepancy' between experimental results and theory, students will have shown that they were able to question the theory and revisit it to explore the 'fine print' associated with it.

Section 3 – Student Learning Experience

3.1 Did this experiment help you to understand the theory and concepts of the topic? If so, how, or if not, why not?

S: Yes, I learned that the Debye-Hückel limiting law only applies for I<0.01, and that a reaction between 2 ions of the same charge (-ve in this case) can be catalysed by the presence of more ions of the opposite charge (+ve in this case) ie. by an increase in ionic strength.

3.2 How is this experiment relevant to you in terms of your interests and goals?

S: The experiment shows an indirect method for measurement of the time taken for a concentration change which is always useful to know.

3.3 Did you find this experiment interesting? If so, what aspects of this experiment did you find of interesting? If not, why not?

S: It wasn't too bad, but it took ages to equilibrate everything.

3.4 Can the experiment be completed comfortably in the allocated time? Is there time to reflect on the tasks while performing them?

S: Easily; there is lots of time to think about the experiment while the solns are equilibrating.

3.5 Does this experiment require teamwork and if so, in what way? Was this aspect of the experiment beneficial?

S: There wasn't enough room in the water bath to equilibrate all of the solutions at the same time, so you had to work together to organise space in the water bath and when you were going to do each mix. This worked OK.

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Appendix 1:

An achievement test

A. Statements, for which each answer was "true" or "false". In addition, the students had to explain their answers.

a. Ionic material does not conduct in the solid phase, since in this phase there are no ions. True / False

b. Aluminum chloride conducts in the solid phase, since it does not consist of ions. True / False

c. Copper chloride conducts in the solid phase due to the flow of the electrons. True / False

d. Each solution conducts electricity. True / False

e. The melting point of an ionic solution depends on the charge of the electrons. True / False

B. Open-ended questions

I. Write the empirical formula of the ionic materials written below:

a. Potassium Iodide
b. Magnesium Phosphate
c. Barium Oxide
d. Calcium Sulfate
e. Calcium Hydroxide
f. Sodium Carbonate

II. Complete and balance the following processes:

1. $KI_{(s)} \xrightarrow{H_2O(l)}$
2. $ZnSO_{4(s)} \xrightarrow{H_2O(l)}$
3. $CuBr_{2(s)} \xrightarrow{H_2O(l)}$
4. $Na_3PO_{4(s)} \xrightarrow{H_2O(l)}$
5. $K_2CO_{3(s)} \xrightarrow{H_2O(l)}$

III. "Copper and copper chloride:

1. Are they solid at room temperature?
2. Can they conduct electricity at room temperature?" Explain!

Continuation from page 8: An APCELL Experiment

3.6 Did you have the opportunity to take responsibility for your own learning, and to be active as learners?

S: To get a decent mark in any prac you have to understand what it's about; asking questions, rereading the prac. notes and reading through the relevant sections of the textbook are essential in doing this. The opportunity to do all of these things was certainly there; the demonstrators were especially helpful.

3.7 Does this experiment provide for the possibility of a range of student abilities and interests? If so, how?

S: The experiment was specific; it taught you about the Debye-Hückel limiting law and a bit of qualitative activated complex theory. The calculations were reasonably challenging (but far from impossible) and for an extra challenge, you could derive the equations given in the prac. manual*.

*(*Note, the Student Notes have since been modified to incorporate the majority of relevant derivations.)*

3.8 Did the laboratory notes, demonstrators' guidance and any other resources help you in learning from this experiment? If so, how?

S: The prac notes were adequate for the preparation and write-up of the experiment and the demonstrators were especially helpful.

3.9 Are there any other features of this experiment that made it a particularly good or bad learning experience for you?

S: I certainly remembered that the Debye-Hückel limiting law doesn't apply when $I>0.01$, so it was useful in that respect.

3.10 What improvements could be made to this experiment?

S: I like the idea of including Assessment Criteria and intended learning outcomes in the prac. notes – it means you have some idea of what you have to look out for as the experiment proceeds*.

*(*Note, this pertains to a previous version of the Student Notes, where this information was not included - at that time, this information was only beginning to be incorporated into some experiments. It has subsequently been included in the Student Notes for this experiment.)*

3.11 Any Other Comments

none