FIRST ORDER CHEMICAL KINETICS: INVERSION OF SUCROSE

References:
See 'References to Experiments'
Please note that since the $a_{\infty}$ is determined, the Guggenheim method is not needed.

Objectives:
To measure:
• The rate of inversion of sucrose and its dependence on temperature
To compute:
• The pseudo-first order rate constant for the acid-catalyzed inversion of sucrose
• The activation energy, pre-exponential factor, $\Delta_S^\dagger$ and $\Delta_H^\dagger$
• The half life of the reaction at each temperature.
To know the following and their interrelations:
• Reaction order and pseudo-order
• Rate equation for first order reactions
• Rate and rate constant
• Half life of a first order reaction
• Arrhenius equation including activation energy and pre-exponential factor
• $\Delta_S^\dagger$ and $\Delta_H^\dagger$
• Optical activity

Materials and Apparatus:
Sucrose
3.0 N HCl
Polarimeter (Na lamp)
Water-jacketed polarimeter tubes
Constant temperature circulating baths
Timer

Background:
Know the following and their interrelations:
• Reaction order
• Rate equation for first order reactions
Rate and rate constant
Half life of a first order reaction
Arrhenius equation including activation energy and pre-exponential factor
\( \Delta S^\ddagger \) and \( \Delta H^\ddagger \)
Optical activity

Procedure:

Week One
1. Into a 100-ml vol. flask place 15 to 20 grams of sucrose (weighed accurately on an analytical balance) add 50 ml of room temperature (25°C) distilled water and shake to dissolve. Do not dilute to the mark until step (3).
2. Fill the polarimeter tube with distilled water and calibrate each polarimeter for a zero reading correction.
3. Pipet 25 ml of room temperature (25°C) 3 N HCl into the sucrose solution. Start the timer. Add room temperature distilled water to the 100 ml mark and mix thoroughly. Rinse the polarimeter tube (connected to the 25°C bath) sufficiently with the sucrose solution and fill with the solution. Start measurements of the angle of rotation, \( \alpha_t \), vs. time as soon as possible and repeat periodically (every 3 to 5 minutes or after \( \alpha \) has changed by about one degree) for at least two hours. **CAUTION:** HCl is corrosive
4. Repeat steps 1-3 at two higher temperatures (30° and 35°) using the available water-jacketed polarimeter tubes and thermostated solutions at the indicated temperatures. Record the actual temperature of each circulating bath and hence of the reactions in the corresponding polarimeter tubes to 0.01°C.
   - The three runs may be made consecutively or performed simultaneously. For simultaneous runs start the lower temperature first since the reaction will be slower. This has two advantages:
     a) it provides experience in measurements when time is not as critical,
     b) after the reaction is slowed down (after 30 minutes) then the readings at the higher temperatures can be sandwiched in between those at the lower temperature with relative ease.
5. Save the three solutions (remaining in the vol. flasks) until the second week
6. Rinse the polarimeter tubes thoroughly with distilled water at the end of the laboratory session (when you are through) and clean up any spilled solutions on the bench top, polarimeter and other equipment used.

Week Two
5. Measure the optical rotation, \( \alpha_\infty \), of the saved solutions

Treatment of Data:
1. Plot the data for each temperature as \( \ln (\alpha_t - \alpha_\infty) \) versus time. This can be done since the concentration at time \( t \), \( C_t \), is proportional to \( (\alpha_t - \alpha_\infty) \) and the initial concentration, \( C_\infty \), is proportional to \( (\alpha_0 - \alpha_\infty) \). Thus for a 1st-order reaction the integrated form of the rate equation is:

\[
\ln \frac{C_t}{C_\infty} = \ln \frac{(\alpha_t - \alpha_\infty)}{(\alpha_0 - \alpha_\infty)} = -kt
\]

or
\[ \ln(\alpha_t - \alpha_\infty) = \ln(\alpha_0 - \alpha_\infty) - kt \]

2. Determine the rate constants at each temperature from the slopes of the lines.

3. Determine the half-life of the reaction at each temperature from the rate constants.

4. Plot the ln of the rate constants versus 1/T; from the slope of the line calculate the activation energy, and calculate the pre-exponential factor from the intercept.

5. Calculate the rate of hydrolysis of sucrose in M/s for a concentration of 0.500 M sucrose and your concentration of acid at one temperature.

6. Calculate the $\Delta S^\dagger$ and $\Delta H^\dagger$ of activation at 25°C. (Hint: these values can be determined from the Arrhenius parameters.)

7. Include in the discussion consideration of the question: is the reaction truly first order, and if not, why not?

**Error Analysis:**

1. From the standard deviations of and intercept slope (from linear least-squares analysis), calculate the standard deviation of $E_a$ and $A$.

2. Discuss sources of systematic error in this experiment, and suggest ways of eliminating as many of them as possible.