Experiment 5.
Thermodynamics of the Dissolution of Borax

Experimental Procedure

CONTENTS

OBJECTIVES

- To standardize a hydrochloric acid solution
- To determine the solubility product of borax as a function of temperature
- To determine the standard free energy, standard enthalpy, and standard entropy changes for the dissolution of borax in an aqueous solution

INTRODUCTION

Standard Free Energy, Enthalpy, and Entropy Changes

- **The free energy change (Gibbs free energy)** of a chemical process is proportional to its equilibrium constant according to the equation

$$\Delta G^\circ = -RT \ln K$$

- Additionally, the free energy change of a chemical process is also a function of the enthalpy change and the entropy change of the process

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

- **Enthalpy change** – Amount of heat evolved or absorbed in a reaction carried out at constant pressure.
- **Entropy change** – Related to the randomness. Sum of the change in the reservoir, the system or device, and the surroundings.

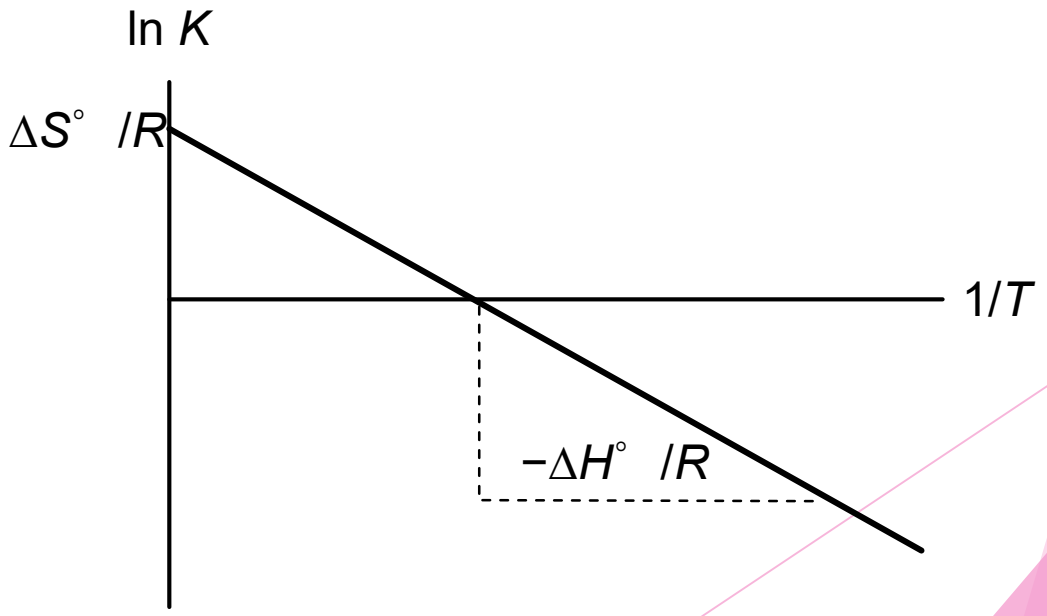
$\Delta G^\circ = -RT \ln K$

When the two free energy expressions are set equal, then

$$-RT \ln K = \Delta H° - T\Delta S°$$

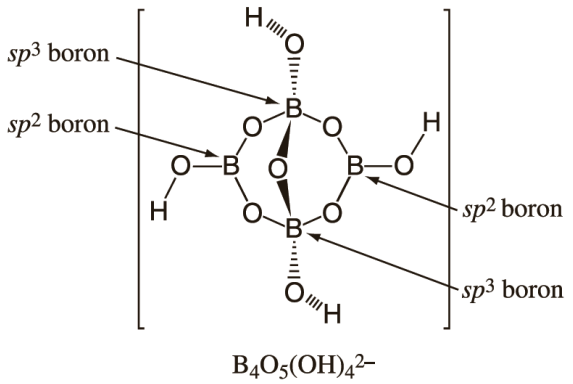
Rearranging and solving for ln *K*,

$$\ln K = -\frac{\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R} \approx y = mx + b$$



The Borax System

- Borax (Sodium tetraborate decahydrate): $Na_2B_4O_5(OH)_4{\cdot}8H_2O$



$B_4O_5(OH)_4^{2-}$

- Solubility Product & Molar Solubility (S) of Borax:

$$Na_2B_4O_5(OH)_4{\cdot}8H_2O(s) \rightleftharpoons 2\ Na^+(aq) + B_4O_5(OH)_4^{2-}(aq) + 8\ H_2O(l)$$

$$K_{sp} = [Na^+]^2[B_4O_5(OH)_4^{2-}] = (2S)^2{\cdot}S = 4S^3$$

The molar solubility of borax can be determined empirically by measuring the molar concentration of the $B_4O_5(OH)_4^{2-}$ in a saturated borax solution with a titrimetric analysis.

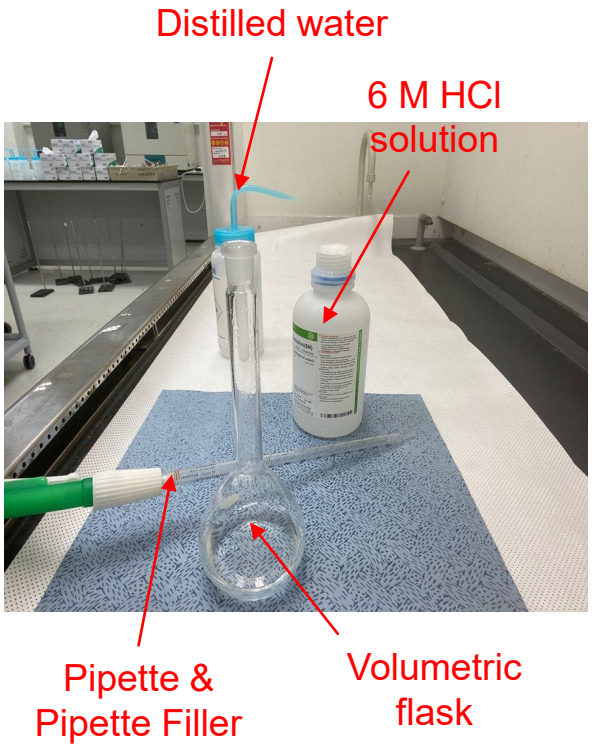
$$B_4O_5(OH)_4^{2-}(aq) + 2\ H^+(aq) + 3\ H_2O(l) \rightleftharpoons 4\ H_3BO_3(aq)$$

EXPERIMENTAL PROCEDURE & RESULT VIDEOS

A. Standardization of HCl Solution

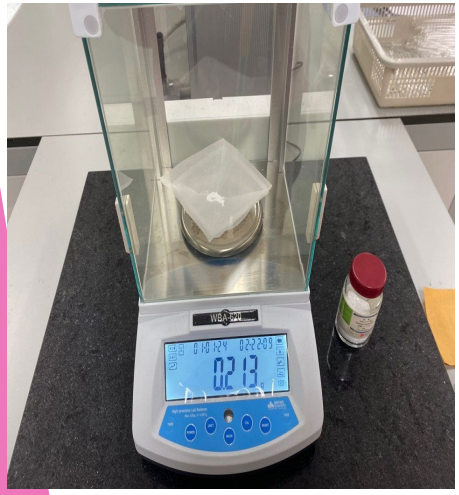
1. Prepare the HCl solution.

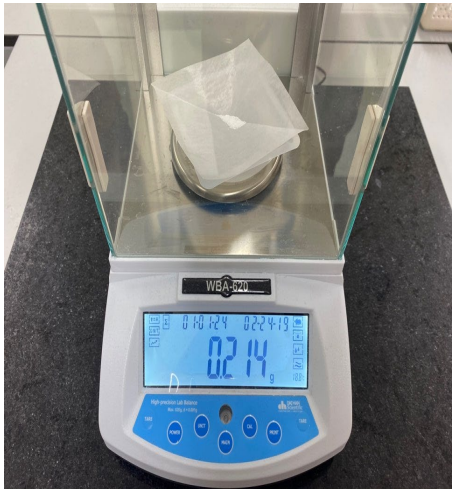
Prepare 0.20 M HCl solution in a 250 mL volumetric flask from 6 M HCl solution per experimental group.



2. Prepare the primary standard.

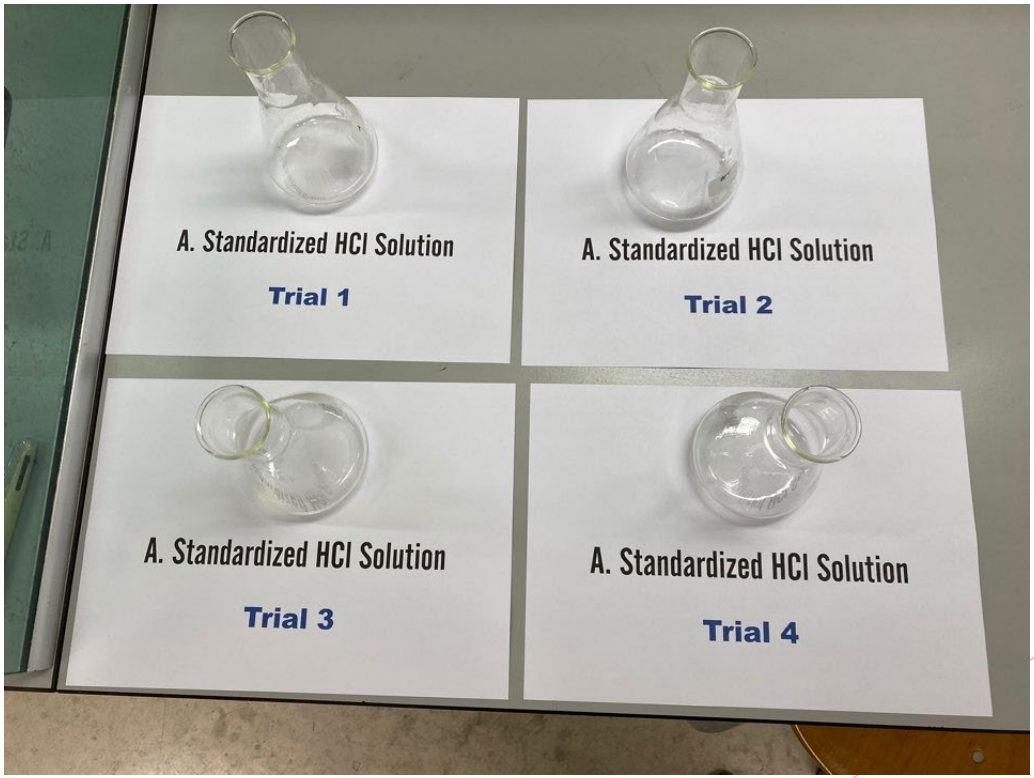
Calculate the mass of sodium carbonate that neutralizes 20 mL of 0.20 M HCl at the stoichiometric point. Measure this mass on a tared piece of weighing paper or dish.





Transfer sodium carbonate to a 125 mL Erlenmeyer flask.

Prepare at least three samples of sodium carbonate for the analysis of the HCl solution.



3. Prepare the buret.

Clean a buret.

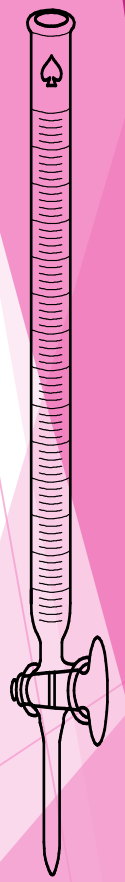
① With the stopcock closed, add some distilled water to the buret and make sure the water contacts all the inside part of the buret.

② Open the stopcock and let the water drain.

③ Close the stopcock again and add 3–5 mL of solution. Tip the buret so that the inside of the buret can be rinsed with the solution.

④ Drain the solution.

⑤ Repeat ③–④ few times.

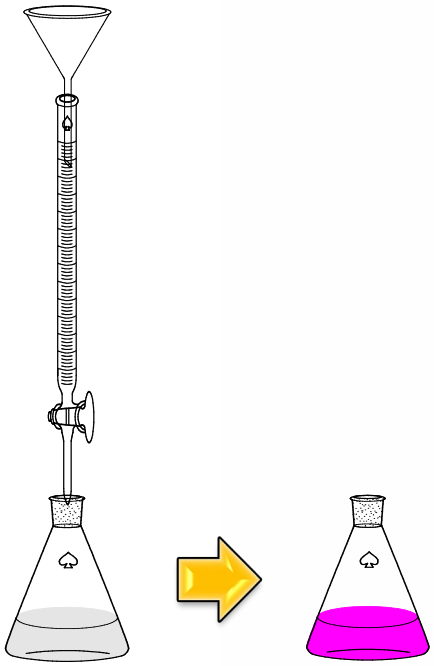


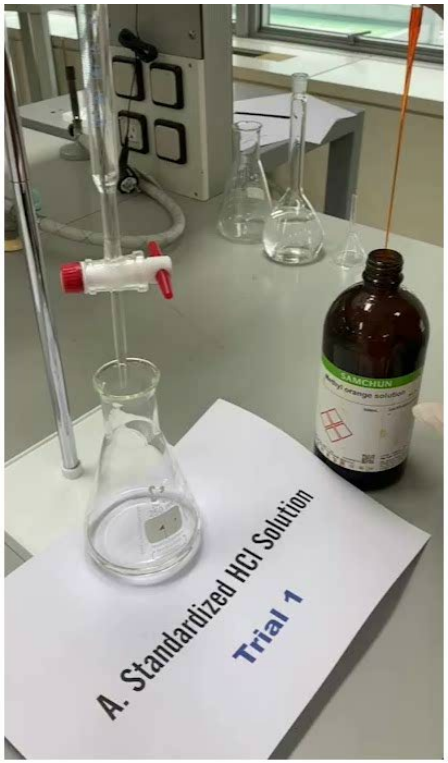
Use a clean funnel to fill the buret with the HCl solution.

Record the volume of HCl solution in the buret.

4. Titrate the primary standard

To each solid sodium carbonate sample, add ~50 mL of deionized water and several drops of methyl orange indicator. Place a sheet of white paper beneath the Erlenmeyer flask.

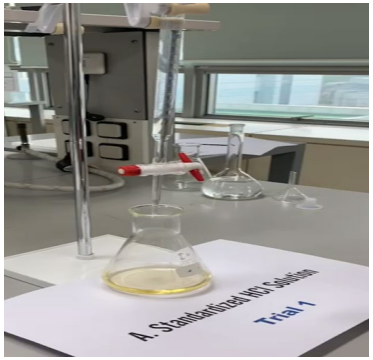
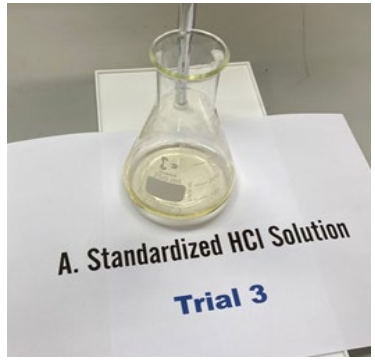
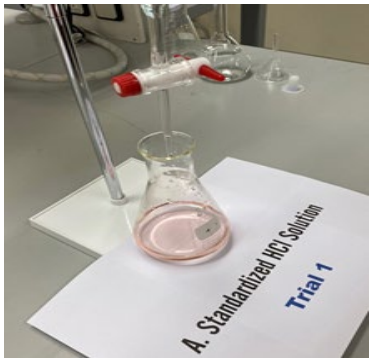
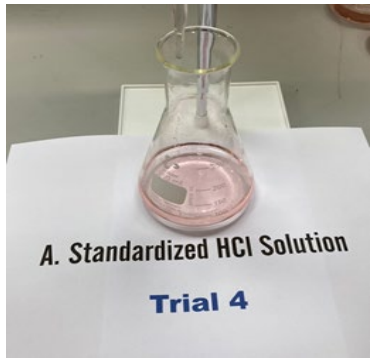




Dispense the HCl solution from the buret, swirling the Erlenmeyer flask during the addition. Carefully add additional HCl titrant until the endpoint is reached and the red–orange color persists for 30 s (a color change caused by the addition of one additional drop of the HCl solution from the buret). Stop the addition of the HCl titrant. After 10–15 seconds, record the volume of HCl in the buret.

5. Repeat the analysis & Do the calculations

Repeat three more analyses and calculate the molar concentration of the prepared HCl solution.

Before				
After				
Trial	1	2	3	4

B. Preparation of Borax Solutions

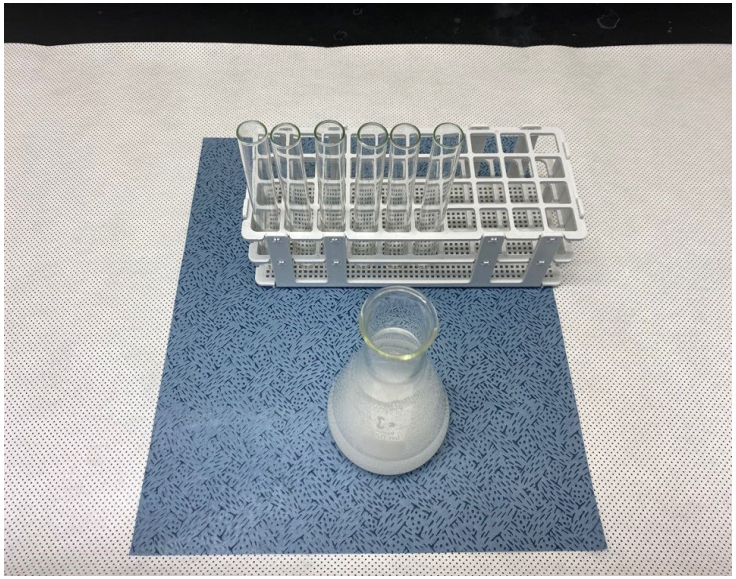
1. **Prepare stock solution of borax.**

Use a 250 mL Erlenmeyer flask, **add 35 g of borax to 100 mL of deionized water.** Agitate the mixture for several minutes to prepare the saturated solution.

Use a 250 mL Erlenmeyer flask, **add 35 g of borax to 100 mL of deionized water.** Agitate the mixture for several minutes to prepare the saturated solution.

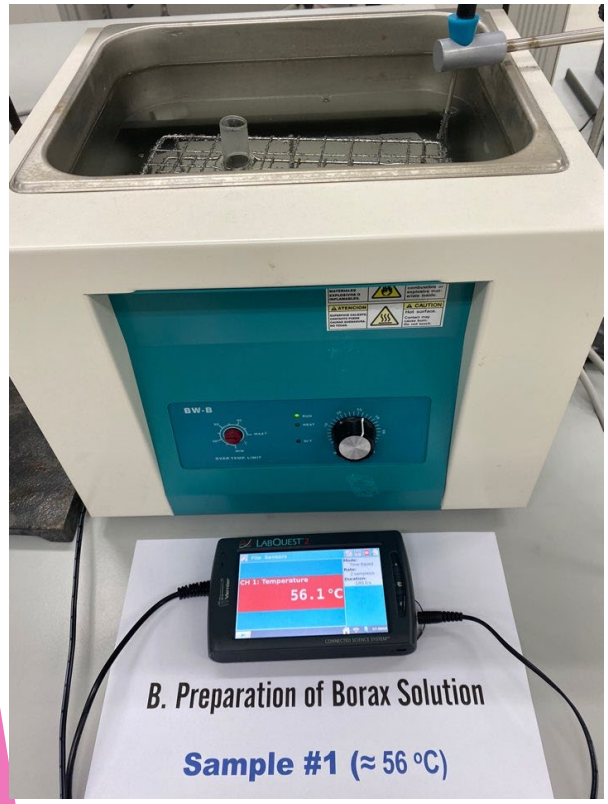
2. Prepare the test solutions of borax.

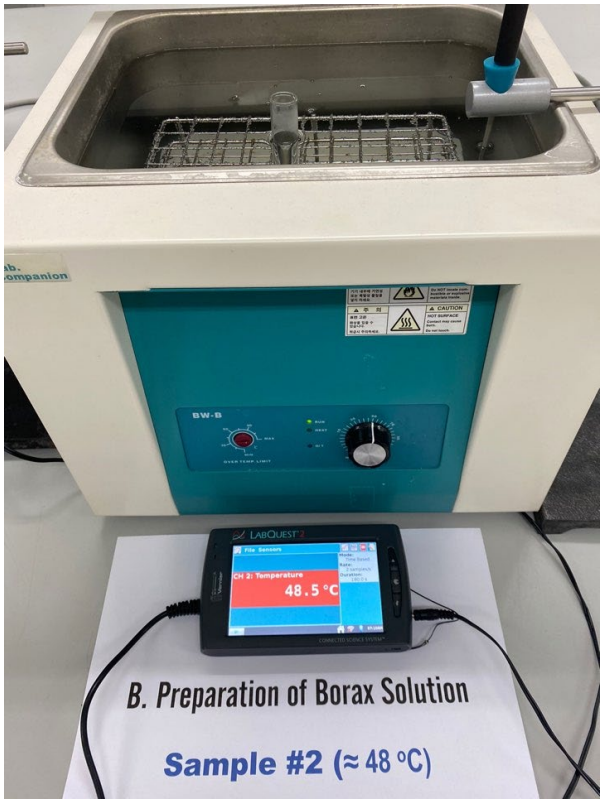
Label a six clean, medium-sized test tubes (Test tube # and experimental group). Again, thoroughly agitate the borax stock solution and then, half-fill this set of medium-sized test tubes with the stock solution.

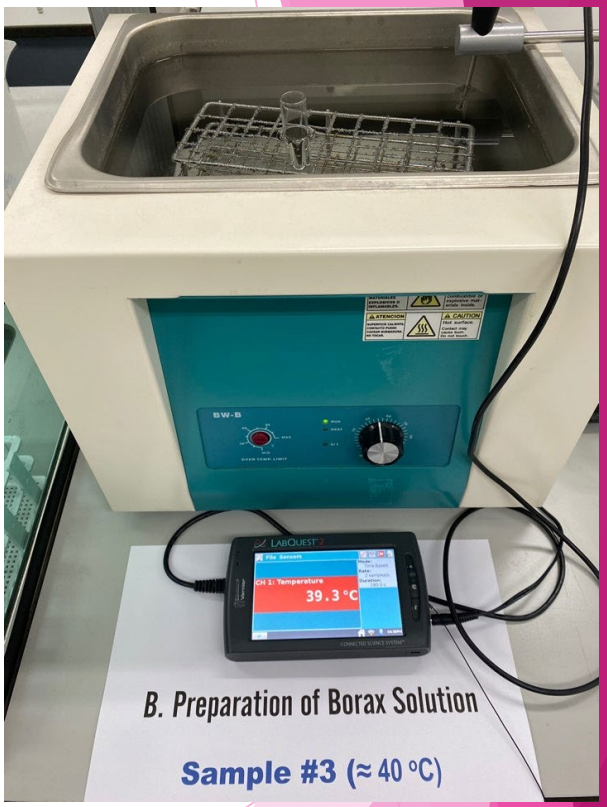


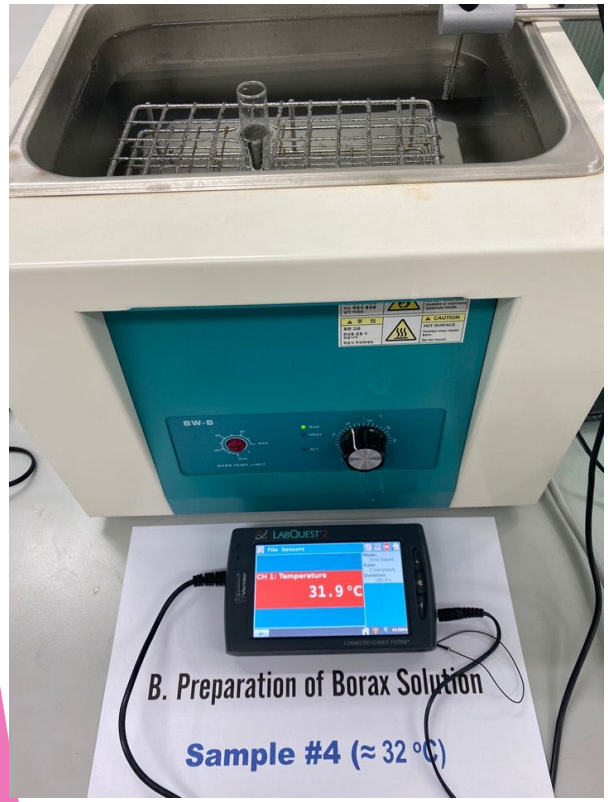
Place the test tubes in the respective baths:

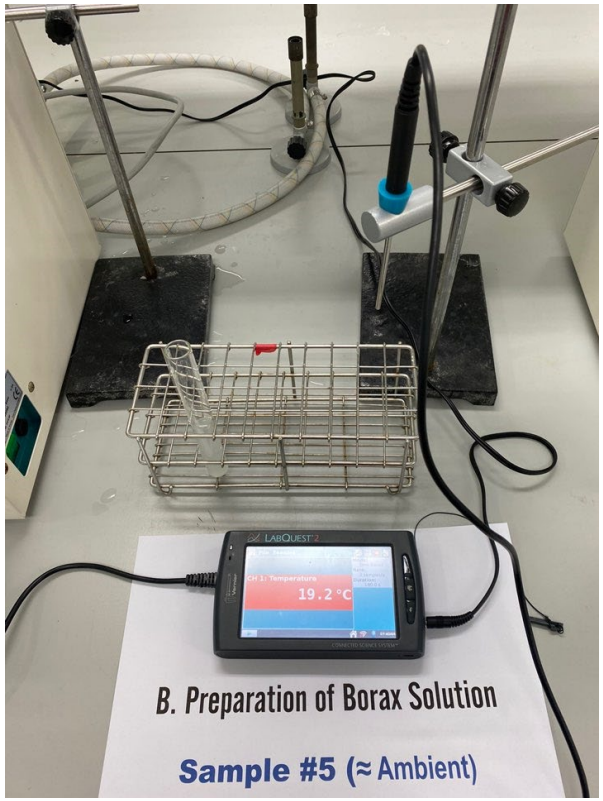
Sample 1 ≈ 56 ℃, Sample 2 ≈ 48 ℃, Sample 3 ≈ 40 ℃, Sample 4 ≈ 32 ℃, Sample 5: Ambient, Sample 6 ≈ 5 ℃


LABQUEST 2
CH 1: Temperature
56.1 °C
B. Preparation of Borax Solution
Sample #1 (≈ 56 °C)


LABQUEST 2
CH 2: Temperature
48.5 °C
B. Preparation of Borax Solution
Sample #2 (≈ 48 °C)


LABQUEST 2
CH 1: Temperature
39.3 °C
B. Preparation of Borax Solution
Sample #3 (≈ 40 °C)


LABQUEST 2
CH 1: Temperature
31.9 °C
B. Preparation of Borax Solution
Sample #4 (≈ 32 °C)


LABQUEST 2
CH 1: Temperature
19.2 °C
B. Preparation of Borax Solution
Sample #5 (≈ Ambient)


LABQUEST 2
CH 1: Temperature
4.3 °C
B. Preparation of Borax Solution
Sample #6 (≈ 5 °C)

3. Prepare the saturated solutions of borax.

a. Saturate the solutions

Occasionally agitate the test tubes in the baths to make solution in each tube be saturated. Solid borax should always be present—add more solid borax if necessary.

b. Allow sample to settle (*not* change temperature)

Allow the borax to settle until the solution is clear (this will require several minutes, be patient!) and has reached thermal equilibrium. Allow 10–15 minutes for thermal equilibrium to be established.

C. Analysis of Borax Test Solutions

1. Transfer the samples.

a. Prepare for sample transfer.

Set up and label a set of six clean labeled 250 mL Erlenmeyer flasks.

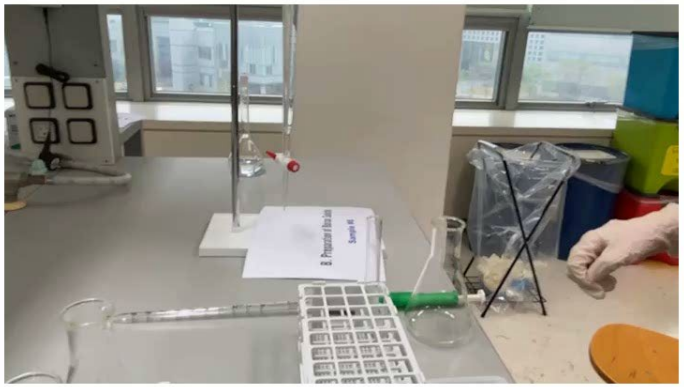
b. Transfer the samples **with a 5 mL pipette.**

After the sample is clear in the test tube, transfer the solution with a 5 mL pipette to the correspondingly labeled Erlenmeyer flask (Do not transfer any of the solid borax), rinse the pipettes with two or three ~5 mL portions of warm, deionized water (~55 ° C) and combine the washings with the sample.

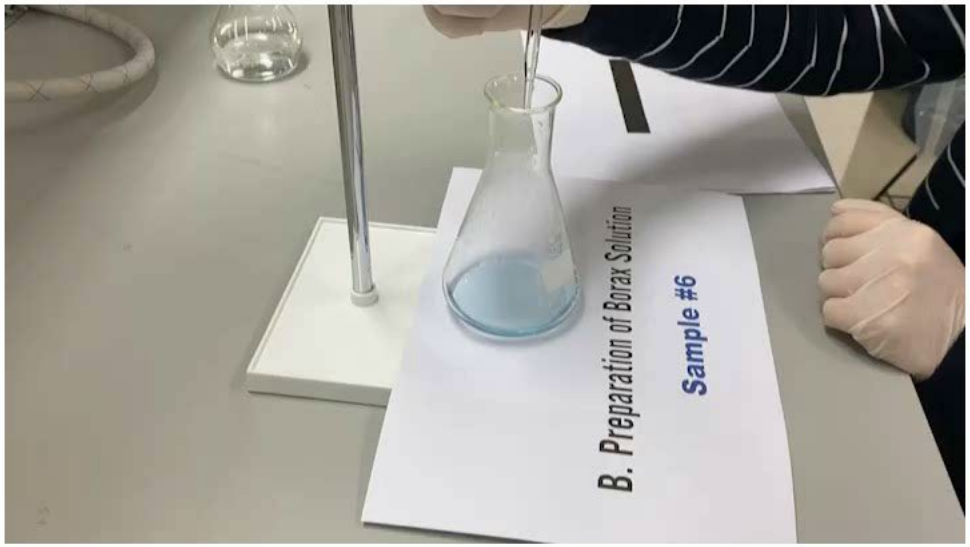
(Caution! Borax is stable in aqueous solutions at temperatures less than 60 ° C; at higher temperatures, some dehydration of the $B_4O_5(OH)_4^{2-}$ anion occurs.)

2. Titrate the samples.

Dilute each sample to about 25 mL with warm, deionized water. Add 2–3 drops of bromocresol green.



Titrate each of the six samples **to a yellow endpoint** with the standardized HCl solution prepared in Part A. **Remember to record the buret readings** before and after each analysis of a sample.



D. Data Analysis

Six repeated calculations are required to establish the data plot for the determination of ΔH° and ΔS° for the dissolution of borax. The lengthy task of completing the calculations and for minimizing errors in the calculations can be reduced with the use of an Excel spreadsheet. The data from the calculations can then be plotted using the embedded graphing capabilities of Excel.

1. Calculate the molar solubility of borax at each of the measured temperatures.
2. Calculate the solubility product of borax at each of the measured temperatures.
3. Plot the natural logarithm of the solubility product versus the reciprocal temperature $1/T$ (K^{-1}) for each sample and draw the best straight line.
4. Determine the slope of the linear plot equal to $-\Delta H^\circ / R$ and calculate the standard enthalpy of solution for borax.
5. Determine the y-intercept (at $x = 0$) of the linear plot equal to $\Delta S^\circ / R$ and calculate the standard entropy of solution for borax.

REPORT SHEET

Thermodynamics of the Dissolution of Borax

A. Standardized HCl Solution

Calculate the mass of sodium carbonate sample required in Part A.3.

	Trial 1	Trial 2	Trial 3	Trial 4
1. Tared mass of Na_2CO_3 (*g*)	( )	( )	( )	( )
2. Moles of Na_2CO_3 (*mol*)	( )	( )	( )	( )
3. Buret reading, *initial (mL)*	( )	( )	( )	( )
4. Buret reading, *final (mL)*	( )	( )	( )	( )
5. Volume of HCl added (*mL*)	( )	( )	( )	( )
6. Moles of HCl added (*mol*)	( )	( )	( )	( )
7. Molar concentration of HCl (*mol/L*)	( )	( )	( )	( )
8. Average molar concentration of HCl (*mol/L*)		( )		

B. Preparation of Borax Solution

Sample number	1	2	3	4	5	6
1. Volume of sample (*mL*)	( )	( )	( )	( )	( )	( )
2. Temperature of sample (°C)	( )	( )	( )	( )	( )	( )

C. Analysis of Borax Test Solutions

Sample number	1	2	3	4	5	6
1. Buret reading, *initial (mL)*	( )	( )	( )	( )	( )	( )
2. Buret reading, *final (mL)*	( )	( )	( )	( )	( )	( )
3. Volume of HCl added (*m*L)	( )	( )	( )	( )	( )	( )

D. Data Analysis

Express all calculated values with the correct number of significant figures.

Sample number	1	2	3	4	5	6
1. Temperature, *T (K)*	( )	( )	( )	( )	( )	( )
2. $1/T\ (K^{-1})$	( )	( )	( )	( )	( )	( )
3. Moles of HCl used (*mol*)	( )	( )	( )	( )	( )	( )
4. Moles of $B_4O_5(OH)_4^{2-}$ (*mol*)	( )	( )	( )	( )	( )	( )
5.$[B_4O_5(OH)_4^{2-}]$ (*mol/L*)	( )	( )	( )	( )	( )	( )
6. Molar solubility of borax (*mol/L*)	( )	( )	( )	( )	( )	( )
7. Solubility product, K_{sp}	( )	( )	( )	( )	( )	( )
8. ln K_{sp}	( )	( )	( )	( )	( )	( )
9. $-\Delta H^\circ$ /*R* (from data plot)			( )			
10. $-\Delta S^\circ$ /*R* (from data plot)			( )			
11. $-\Delta H^\circ$ (*kJ/mol*)			( )			
12. $-\Delta S^\circ$ (*J/mol·K*)			( )			
13. $-\Delta G^\circ$ (kJ), at 298 K			( )			