

Enthalpy of Hydration and Solution

INSTRUCTOR RESOURCES

By

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LEARNING OBJECTIVES:

- Qualitatively correlate the ΔH_{soln} of several compounds with their properties such as ionic charge, ionic size, etc.
- To quantitatively determine the enthalpy of solvation of MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.
- To quantitatively determine the enthalpy of the water of hydration in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

PROCEDURAL OUTLINE

- Qualitatively determine Q_{soln} of ammonium nitrate, sodium chloride, lithium chloride, sodium hydroxide, sodium nitrate, sodium sulphate, and 0.50 mL of conc. sulphuric acid.
- Quantitatively determine Q_{soln} of 2, 4, 6 and 8 g of MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
- Calculate Q_{soln} per gram, and ΔH_{soln} per mole of MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from linear curve fits of the 2,4,6 and 8 g experiments.
- Calculate the $\Delta_{\text{Hydration}}$ for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Name _____ Section _____ Date _____

Enthalpy of Hydration and Solution

Report Sheet

Table 1 : Data for Qualitative Experiments:

Before coming to lab, obtain the following information from the handbook of Chemistry and Physics (look under "ionic radii, crystal") the Sargent Welch Periodic Chart, etc., along with any other pertinent information that might be useful in understanding the results of this experiment.

Compound	L'IT	Cation Size	Cation Charge	Anion Size	Anion Charge	# M Core electrons	(Any other parameters)
LiCl				1.67			
NaCl				1.67			
NaOH				1.19			
NaNO ₃				1.65			
Na ₂ SO ₄				2.44			
NH ₄ NO ₃				1.65			
c H ₂ SO ₄				2.44			
MgSO ₄				2.44			

Table 2: Data for Quantitative Experiments:

MgSO ₄						MgSO ₄ • 7H ₂ O					
Mass	T1	row #	T2	row #	ΔT @ mid row #	Mass	T1	row #	T2	row #	ΔT @ mid row #

ΔH_{soln} MgSO₄ _____

ΔH_{soln} MgSO₄ • 7H₂O _____

Δ_{Hydration} MgSO₄ • 7H₂O _____

Name _____ Section _____ Date _____

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Report Sheet (page 2)

Calculations for ΔH_{soln} MgSO_4 :

Calculations for ΔH_{soln} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Calculations for $\Delta_{\text{Hydration}}$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Name _____ Section _____ Date _____

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Questions/Problems

1. What is the sign of the ΔH_{soln} for each of the salts used in this experiment?

Cmpnd	NH ₄ NO ₃	NaCl	NaOH	NaNO ₃	Na ₂ SO ₄	c H ₂ SO ₄	MgSO ₄	MgSO ₄ • 7H ₂ O
Sign								
Major ion								

2. Since the concentration of each solution is about the same, and the solvent is the same, determine which ion of each compound has the major influence on this sign and indicate this ion in the bottom row of the above table.
3. What reaction is occurring with each of these compounds? Write out the net ionic equation for each compound. Be sure to include the enthalpy information!

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Questions/Problems (Page 2)

4. By examining the sign, relative magnitude of the ΔH_{soln} and the data in Table 1 above for each compound investigated, correlate this information and explain why each of the major contributing ions produces the result observed.

BE SURE TO INCLUDE THE APPROPRIATE GRAPHS AND TABLES, AND THE ANSWERS TO THE QUESTIONS WITHIN THE EXPERIMENT AS WELL AS THE ABOVE QUESTIONS IN YOUR REPORT.

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Tips and Traps

1. The density of each of the salts varies from 1.73 for ammonium nitrate to 2.68 for sodium sulfate, so if students weigh out the correct amount of **NaCl**, to determine the amount, and are careful to get about that same sample size of each salt on a spoon spatula, a good qualitative comparison can be achieved.
2. Everything should be prepared prior to each measurement, and salt samples should be obtained **right before** their ΔH_{soln} is to be measured so that they do not sit in the air and pick up moisture.
3. Each of these salts should be oven dried in a beaker covered with a watch glass for two hours at the temperature indicated, stirring about every half hour, according to the following temperatures. Some of the salts are particularly hygroscopic, and if they are particularly damp, it may take more heating time to dry them. Keep in tightly capped containers thereafter.

Compound	Dry at
ammonium nitrate	100 °C
sodium hydroxide	100 °C
sodium sulfate (anhydrous)	100 °C
sodium chloride	100 °C
sodium nitrate	100 °C
magnesium sulfate anhydrous	200 °C
magnesium sulfate heptahydrate	100 °C
conc. sulphuric acid	DO NOT DRY

4. I found it particularly helpful to set up individual jar sets for each lab section so that all sections have fresh samples to work with.
5. Students should be instructed to wash and dry their spoon spatulas between each sample so that there will not be cross contamination of the samples.
6. Stirring is critical in this lab. Magnetic stirrers work best, and stirring should be vigorous without splashing
7. Make sure that the salts are added to the water in such a manner that they do not stick to the sides of the Styrofoam cup.
8. The temperature probe must be *in* the solution without touching the bottom of the container or the magnetic stir bar.
9. An alternative method for supporting the foam cups is a suitable iron ring (3-inch).
10. If temperature drift is observed after salt addition, extrapolation of temperature to the time of mixing will provide a more reliable T_f value.
11. You need a cover for the foam cups. There are many alternatives; two are suggested below:
 - a. a plastic coffee cup lid.
 - b. a foam square, 3.5" x 3.5" x 0.5" with a hole in the middle for the thermistor. A rubber band or small piece of rubber hose around the thermistor will prevent it from slipping through the foam block or the coffee cup cover.
12. The heat capacity for the calorimeter can be experimentally determined if so desired. A common method is based on the heat produced on mixing known amounts of HCl and NaOH.

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Suggested Answers to Report Sheet

Table 1 : Data for Qualitative Experiments:

Before coming to lab, obtain the following information from the handbook of Chemistry and Physics (look under "ionic radii, crystal") the Sargent Welch Periodic Chart, etc., along with any other pertinent information that might be useful in understanding the results of this experiment.

Compound	ΔT	Cation Size (Å)	Cation Charge	Anion Size (Å)	Anion Charge	# M Core electrons	(Any other parameters)
LiCl		0.68	+1	1.67	-1	2	
NaCl		0.97	+1	1.67	-1	10	
NaOH		0.97	+1	1.19	-1	10	
NaNO ₃		0.97	+1	1.65	-1	10	
Na ₂ SO ₄		0.97	+1	2.44	-2	10	
NH ₄ NO ₃		1.33	+1	1.65	-1	13	
c H ₂ SO ₄		v. small	+1	2.44	-2	0	
MgSO ₄		0.82	+2	2.44	-2	10	

Table 2: Data for Quantitative Experiments:

MgSO ₄						MgSO ₄ • 7H ₂ O					
Mass	T1 Start	row #	T2 max	row #	ΔT @ mid row #	Mass	T1 Start	row #	T2 max	row #	T2 max
2	25.62	62	27.75	135	26.69	2	24.23	57	24.01	126	24.13
4	23.58	75	27.55	158	25.56	4	24.67	61	24.00	141	24.38
6	24.66	72	29.99	171	27.32	6	25.15	68	24.26	163	24.71
8	24.83	68	32.16	205	28.50	8	24.86	62	23.71	192	24.28

ΔH_{soln} MgSO₄: **-54.36 kJ/mol**

ΔH_{soln} MgSO₄ • 7H₂O: **+9.91 kJ/mol**

$\Delta_{\text{Hydration}}$ MgSO₄ • 7H₂O: **-64.27 kJ/mol**

Enthalpy of Hydration and Solution

Suggested Answers to Report Sheet (page 2)

Calculations for $\Delta H_{\text{soln}} \text{MgSO}_4$:

$$\begin{aligned}\Delta H_{\text{soln}} \text{MgSO}_4 &= (100\text{g} + \text{g MgSO}_4) * (4.184\text{J/g}^\circ\text{C}) * (\Delta T_2 - \Delta T_1) * 120.4\text{g/mol} * 1 \text{ kJ}/1000 \text{ J} = \text{kJ/mol} \\ &= (100+2)(4.184) * 2.09 * 120.4\text{g/mol} = -53.70 \text{ kJ/mol for 2.00 g sample} \\ &= (100+4)(4.184) * 2.09 * 120.4\text{g/mol} = -52.65 \text{ kJ/mol for 4.00 g sample} \\ &= (100+6)(4.184) * 2.09 * 120.4\text{g/mol} = -54.29 \text{ kJ/mol for 6.00 g sample} \\ &= (100+8)(4.184) * 2.09 * 120.4\text{g/mol} = -54.88 \text{ kJ/mol for 8.00 g sample} \\ \text{Graph gives a slope of } &-54.37 \text{ kJ/mol}\end{aligned}$$

Calculations for $\Delta H_{\text{soln}} \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

$$\begin{aligned}\Delta H_{\text{soln}} \text{MgSO}_4 \cdot 7\text{H}_2\text{O} &= (100\text{g} + \text{g MgSO}_4) * (4.184\text{J/g}^\circ\text{C}) * (\Delta T_2 - \Delta T_1) * 1 \text{ kJ}/1000 \text{ J} = \text{kJ/mol} \\ &= (100+2)(4.184) * (-0.246) * (246.4)\text{g/mol} = 7.69 \text{ kJ/mol for 2.00 g sample} \\ &= (100+4)(4.184) * (-0.612) * 246.4\text{g/mol} = 9.74 \text{ kJ/mol for 4.00 g sample} \\ &= (100+6)(4.184) * (-0.927) * (246.4)\text{g/mol} = 10.03 \text{ kJ/mol for 6.00 g sample} \\ &= (100+8)(4.184) * (-1.206) * (246.4)\text{g/mol} = 9.97 \text{ kJ/mol for 8.00 g sample} \\ \text{Graph gives a slope of } &9.36 \text{ kJ/mol}\end{aligned}$$

Calculations for $\Delta H_{\text{Hydration}} \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

$$\begin{aligned}\Delta H_{\text{hydration}} &= \Delta H_{\text{soln}} \text{MgSO}_4 - \Delta H_{\text{soln}} \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \\ &= -54.37 - (+9.36) = -63.73 \text{ kJ/mol}\end{aligned}$$

Enthalpy of Hydration and Solution

Suggested Answers to Questions/Problems

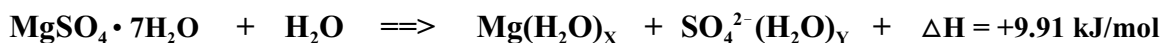
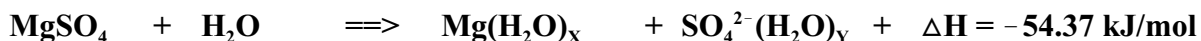
1. What is the sign of the ΔH_{soln} for each of the salts used in this experiment?

Cmpnd	NH_4NO_3	NaCl	NaOH	NaNO_3	Na_2SO_4	c H_2SO_4	MgSO_4	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Sign	+	~ 0	-	+	-	-	-	+
Major ion	NH_4^+ & NO_3^-	Cl^-	OH^-	NO_3^-	SO_4^{2-}	H^+ & SO_4^{2-}	SO_4^{2-}	SO_4^{2-}

2. Since the concentration of each solution is about the same, and the solvent is the same, determine which ion of each compound has the major influence on this sign and indicate this ion in the bottom row of the above table.

See data in table above

3. What reaction is occurring with each of these compounds? Write out the net ionic equation for each compound. Be sure to include the enthalpy information!



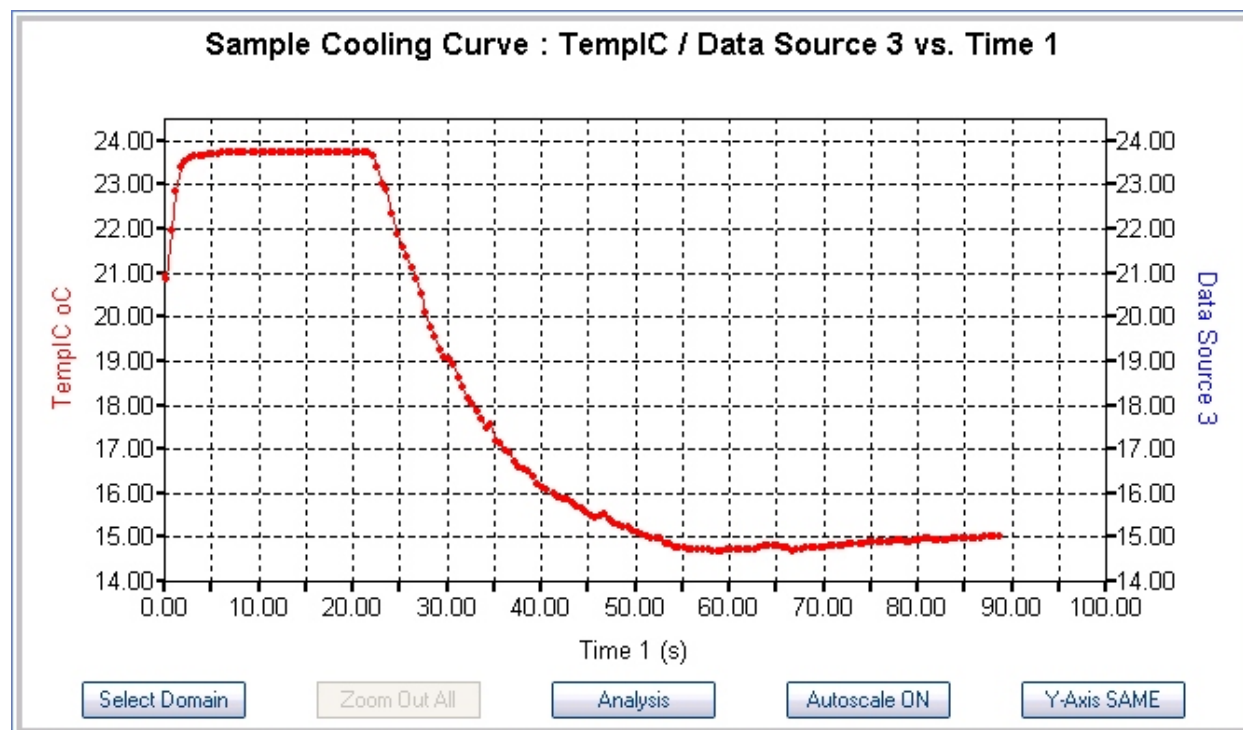
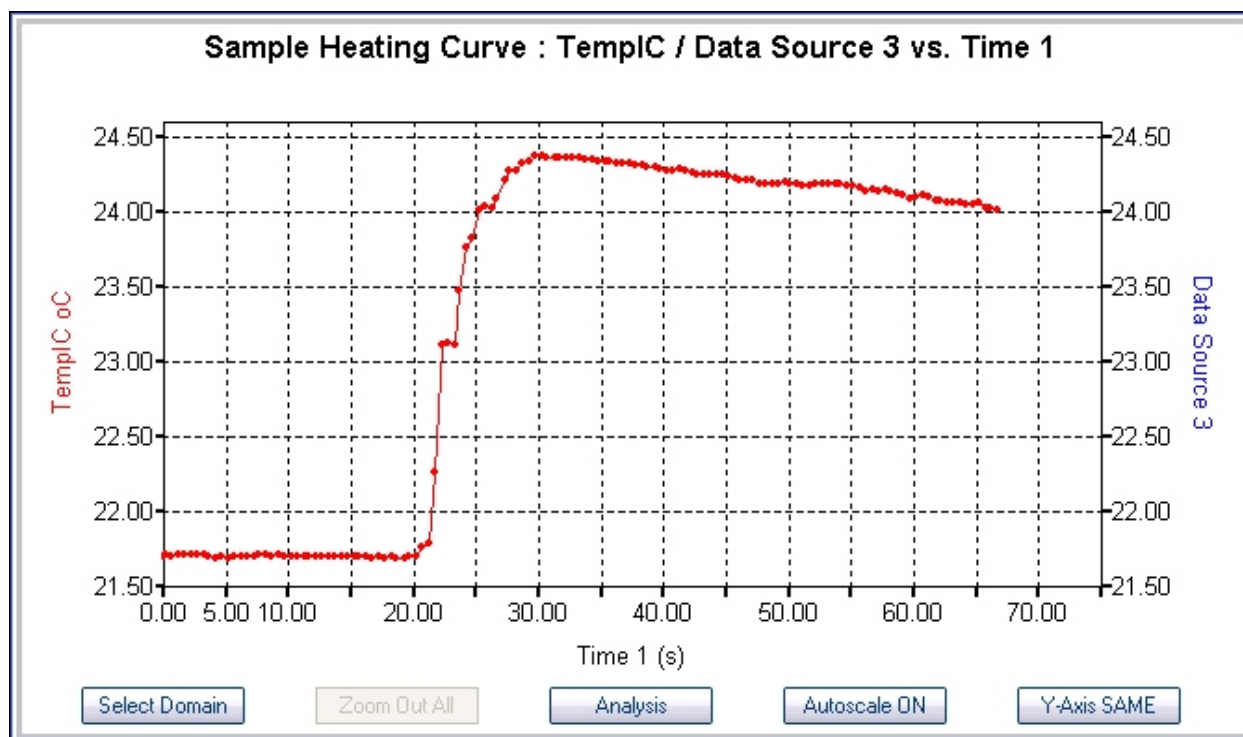
4. By examining the sign, relative magnitude of the ΔH_{soln} and the data in Table 1 above for each compound investigated, correlate this information and explain why each of the major contributing ions produces the result observed.

The energetics of solution can be separated into three components, as discussed in the experimental write-up: (1) the energy to separate the ions from their crystalline state, (2) the energy to separate the solvent molecules, and the energy release by the interactions of the separated ions and the solvent molecules. The greater the charge to size ratio of an ion, the stronger attraction it has for the polar water molecule, termed the ionic hydration energy. If the energy release is greater than the energy required, the process will be exothermic and have a negative ΔH_{soln} . If the reverse is true, the ΔH_{soln} will be positive. The hydrogen, magnesium, lithium and hydroxide and sulfate ions, listed in order of decreasing negative hydration energies, are small and has a large charge to size ratio, releasing relatively large hydration energies, especially the hydrogen, as evidenced by the very negative ΔH_{soln} of the concentrated sulfuric acid. Sodium chloride has essentially zero hydration energy, indicating that the three enthalpies subtract out. Nitrates and have a positive energy of hydration because of their large size, and since ammonium

nitrate has two large ions, its ΔH_{soln} is very positive.

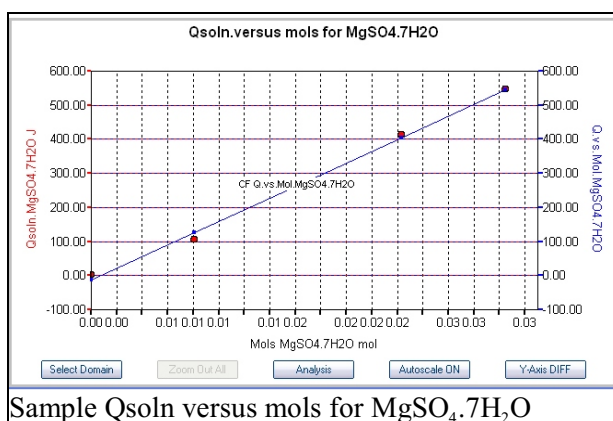
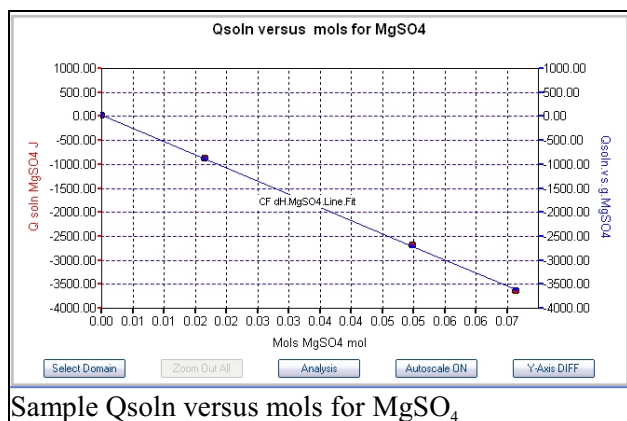
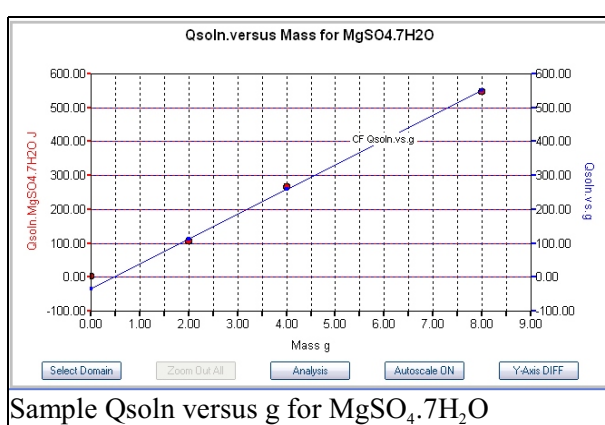
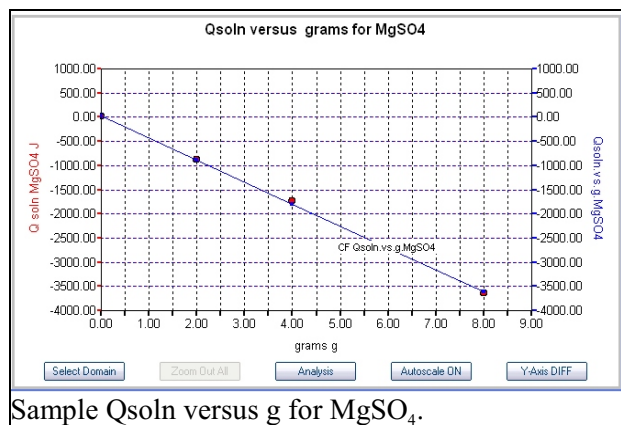
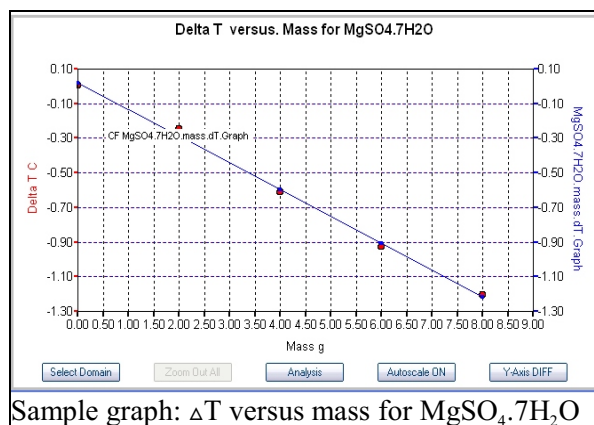
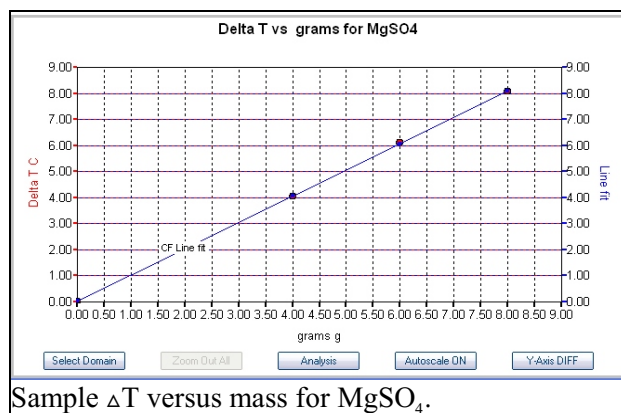
Enthalpy of Hydration and Solution

Sample *MicroLAB* Heating and Cooling Curves



Enthalpy of Hydration and Solution

Sample *MicroLAB* MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ Curves



Enthalpy of Hydration and Solution

Laboratory Preparation (per student station)

Equipment

- a temperature probe
- ring stand
- utility clamp
- two foam cups (nested into a 400 mL beaker to form a calorimeter)
- cover for foam cup
- magnetic stirrer and stir bar
- 100 ml graduated cylinder
- MicroLab interface
- ice (for calibration)
- hot water (for calibration)

Supplies

- weighing paper or weighing boat

Chemicals

Each of these salts should be dried. On the morning of the lab, heat them in the oven in a beaker covered with a watch glass for 2 hours at the temperature indicated. Stir frequently to break up the material and obtain complete removal of unwanted water. Keep in tightly capped containers thereafter. Make a set of separate containers for each lab section.

Compound	Dry at
• 1.5 g of ammonium nitrate	100 °C
• 1.5 g of sodium hydroxide	100 °C
• 1.5 g of sodium sulfate (anhydrous)	100 °C
• 1.5 g of sodium chloride	100 °C
• 1.5 g of sodium nitrate	100 °C
• 25 g of magnesium sulfate anhydrous	200 °C
• 25 g of magnesium sulfate heptahydrate	100 °C
• 1.5 ml conc. sulphuric acid	Do Not Dry

Safety and Disposal

Ammonium nitrate: Irritant to skin, eyes and mucous membranes. Store away from any source of combustion or ignition.

Magnesium sulfate: Low toxicity, may irritate eyes and respiratory tract. Avoid contact with skin, eyes and mucous membranes.

Sodium Chloride: Prudent laboratory practices should be observed. Slightly toxic by ingestion.

Sodium Hydroxide: Avoid body contact. Highly toxic by ingestion. Strong tissue irritant; particularly hazardous to eye tissue. Damage occurs very quickly.

Sodium Sulphate: Prudent laboratory practices should be observed. Substance not considered hazardous.

Sodium Nitrate: Toxic by ingestion. Avoid heat, friction, and contact with organic and combustible substances.

Sulfuric Acid, conc.: Avoid contact with skin, eyes and mucous membranes. Avoid explosive spattering when mixed with water, always add acid to water, never the reverse. Severely corrosive to eyes, skin and other tissues. Toxic; strong skin irritant.