

Experiment

ENTHALPY OF HYDRATION AND SOLUTION

By

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LEARNING OBJECTIVES:

- To qualitatively correlate the ΔH_{soln} of several compounds with their properties such as ionic charge, 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 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

INTRODUCTION:

Many ionic salts contain water molecules that are loosely bound to the salt ions. These water molecules can be driven off from the salt by heating the salt to the appropriate temperature. The stronger the water molecules are bonded to the ions, the higher the temperature necessary to drive them off. The energy of this process is difficult to measure experimentally, however, so we will approach it in a different manner. When a substance is dissolved, it becomes surrounded by a sphere of solvent molecules called the solvation sheath or sphere. The thickness of this solvation sphere depends on the concentration of the solution, the less concentrated the solution, the thicker the solvation sphere. Two solutions of MgSO_4 in water of the same concentration should then have the same thickness of water molecules in the solvation sphere around each ion. For dilute solutions (less than 0.01 Molar) the number of water molecules added by dissolving $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ versus MgSO_4 is sufficiently small that it can be neglected, (very small % error) and therefore it can be assumed, within experimental error, that the solvation sphere is the same in each.

When heat is involved in a chemical reaction, it is generally represented as "q," and can be either exothermic, where heat is released by the system to the surroundings, or endothermic, where heat is absorbed by the system from the surroundings. When this process takes place at constant pressure such as reactions at atmospheric pressure, the heat is referred to as "enthalpy" and given the symbol ΔH . Generally, when ΔH is used, it usually also refers to the amount of heat involved per mole of the compound of interest, here, the solute.

When a substance is dissolved, there are always three energy processes that must be considered, as follows:

1. The solvent molecules must be separated from each other to make room for the solute molecules. This process requires energy, will be termed ΔH_1 , and is positive.
2. Next, the solute molecules or ions must be separated from each other to be able to fit in between the solvent molecules. This process also requires energy, will be termed ΔH_2 , and is also positive.
3. Last, there must be an attractive interaction between the solute molecules or ions and the solvent molecules to supply the energy required for the above two separations, this will be termed ΔH_3 and is negative.

The overall energy of the solution process depends on the relative magnitudes of ΔH_1 , ΔH_2 and ΔH_3 and can be expressed as the algebraic sum in the equation $\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{\text{solvation}}$ where ΔH_{soln} and $\Delta H_{\text{solvation}}$ are equivalent terms. Since we are dealing here with all aqueous solutions of ionic compounds of approximately the same concentration, ΔH_1 will remain a constant. Therefore, ΔH_{soln} will depend on the relative energy to separate the ions, ΔH_2 and the interaction of those ions with the water solvent molecules, ΔH_3 .

Another factor that has an influence here is the charge to size ratio of the ions. Water is a polar molecule, with the oxygen end of the molecule being negatively charged, and the hydrogen end being positively charged. When ionic substances are dissolved then, the energy of interaction between the solute and the solvent must come from the attractive forces between the negative end of the water molecule and the solute cations, and the attractive forces between the positive end of the water molecule and the solute anions. Obviously, the more concentrated the charge, i.e., the larger the charge to size ratio, the stronger these forces will be. In this experiment, we will be looking at the influence of this charge to size ratio.

In considering the study involving the two magnesium sulphate compounds, it would seem reasonable to expect that the ΔH_{soln} for MgSO_4 would be larger than the ΔH_{soln} for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ because $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ already has seven waters of hydration associated with it and thus has already released the amount of energy equivalent to those waters of hydration, i.e., the $\Delta H_{\text{hydration}}$. Consequently, assuming the spheres of solvation are the same for approximately the same concentration, as discussed above, accurately measuring the enthalpy of solvation of both MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and then subtracting the ΔH_{soln} for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from the ΔH_{soln} of MgSO_4 should result in an approximation to the $\Delta H_{\text{hydration}}$ for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

EQUIPMENT AND CHEMICALS NEEDED:

You will need to have the following equipment and chemicals available to perform this experiment.

1 - magnetic stirrer with stirring bar

1 - **MicroLAB** interface with a temperature probe

2 - Styrofoam cups with lids with a hole in the lid toward the side for the temperature probe

Electronic balance with at least 0.01 g sensitivity

Split cork, utility clamp and ring stand

A program for the **MicroLAB** interface to collect temperature from the probe, and display it in the **Graph** view, **Digital Display** view and in the **Spreadsheet** view.

1.0 g of ammonium nitrate

1.0 g of sodium chloride

1.0 g of sodium hydroxide

1.0 g of sodium nitrate

1.0 g of sodium sulfate

1.0 g of lithium chloride

1.0 ml conc. sulphuric acid

20 g anhydrous magnesium sulfate

20 g of magnesium sulfate heptahydrate

CAUTIONS:

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.

EXPERIMENTAL PROCEDURE:

1. EQUIPMENT SETUP

- Plug the temperature probe into CAT 5A, then calibrate the probe in an ice bath and in at least two other water baths with temperatures between 0 °C and 60 °C, using a thermometer for calibration.
Remember: your data cannot be better than your calibration
- For the qualitative experiments, name the file after each different compound for later data retrieval. For the quantitative experiments, name the file after the solute and the amount of solute used.

2. QUALITATIVE PROPERTIES OF SOME DISSOLVING COMPOUNDS:

- Add 20 ml of distilled water to a 50-ml beaker, and suspend the temperature probe by a cork in a utility clamp on a ring stand in the beaker at the side and above the stirring bar so that the rotating bar does not strike the temperature probe. Stir the solution moderately.
- Collect temperature data for two to three minutes for the water in the beaker.
- Add an amount equal to the size of a pea of one of ammonium nitrate to the beaker and monitor the graph until the temperature has leveled out and begun to slope up or down for about two or three minutes. Try to keep the amount of the solids approximately equal, and measure them out just before they are to be used so they do not pick up moisture from the atmosphere.
- Repeat steps "a" through "c" for each of the compounds: sodium chloride, lithium chloride, sodium hydroxide, sodium nitrate, sodium sulphate, and 0.50 ml of conc. sulphuric acid.

3. QUANTITATIVE DETERMINATION OF $\Delta H_{\text{solution}}$ AND $\Delta H_{\text{hydration}}$:

- Accurately weigh to 0.01 g approximately 2 g of MgSO_4 to the nearest 0.01 g into a plastic weighing boat.
- Add 100.0 ml of distilled water to a double Styrofoam calorimeter with a lid described above, place it in a 250-ml beaker for stability and place on the magnetic stirrer.
- Insert the temperature probe through the lid and suspend it by a cork clamped in a utility clamp so that it is in the water above the stirring bar. Be careful that the spinning bar does not hit against the temperature probe.
- Using the basic temperature program, collect about one minute of temperature data for the water.
- Slide the lid up on the temperature probe so that you can add the MgSO_4 to the water without removing the temperature probe out of the water.
- Slide the lid back down the temperature probe as soon as the solute has been added and monitor the temperature change on the graph on the screen.
- When the temperature has leveled out and begun cooling down so that you can get a good linear curve

fit on your cooling portion, stop the data collection.

- h. Repeat steps "a" through "g" for 4, 6 and 8 g of anhydrous MgSO_4 .
- I. Repeat steps "a" through "g" for 2, 4, 6 and 8 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

DATA TREATMENT:

- a. From the spreadsheet data for each compound in the qualitative section, obtain the starting temperature, ending temperature and the change in temperature.
- b. Plot a graph of each compound in the qualitative section with the ΔT written on each.
- c. Enter these data into a table of compound vs ΔT and arrange them in order of increasing exothermicity.
- d. What conclusions can be drawn from these observations? What are the similarities and differences in your observations for each compound? What reaction(s) is/are taking place? Can you begin to correlate the amount of change in temperature with the individual ions of the compounds? Give experimental support for your conclusions in your write-up.
- e. Plot a graph of each run in the quantitative section and evaluate each section as follows:
 - (1) Print one of the graphs, then explain on the graph what is occurring in each section of the graph, i.e., the initial flat zone, the rising or falling zone, the plateau, and the downward sloping or upward sloping zone.
 - (2) Place the cursor on a point at the mid point of the steeply changing part of the curve and determine the row number and temperature for this point.
 - (3) Using the domain function, perform a linear curve fit for the initial flat portion of the curve and the constantly falling (for a heating curve) or the constantly rising (for a cooling curve) to obtain the equations for these two domains.
 - (4) Using the linear regression equation for each of the domains calculated above, and the "Interpolate/Extrapolate" function, calculate the temperature for the row number determined in (2) above.
 - (5) Calculate the ΔT for this particular experiment by subtracting the temperature calculated for the initially flat portion for the midpoint row number from the temperature calculated for the constantly falling or rising portion for the midpoint row number.
 - (6) Record this ΔT vs the sample weight in grams in a table.
- f. Repeat steps (1) through (6) for each quantitative run, for both anhydrous MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, tabulating the data by compound.
- g. Print out one of the above graphs for each compound, MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Be sure to label them properly.
- h. Clear the spread sheet and enter the ΔT vs weight data from the table for the anhydrous MgSO_4 , then proceed as follows:
 - (1) In a spreadsheet column, calculate the number of moles of compound for each of the data points.
 - (2) In an adjacent column, calculate the Q_{soln} value for each of the data points. (Assume the specific heat of the solution is $4.184 \text{ J/g}^\circ\text{C}$.)
 - (3) Make a graph of Q_{soln} vs weight, and Q_{soln} vs moles.
 - (4) Do a linear regression through each.

(5) Using the linear regression equation and the "Predict Value" option, calculate the q_{soln} per gram, and the ΔH_{soln} per mole for MgSO_4 .

(6) Print a graph of the data in (3) above with the Predict Value hand printed on the graph.

I. Repeat steps h.(1) through (6) for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

j. From the data from h.(5) and I.(5) calculate the $\Delta H_{\text{hydration}}$ for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. (Write this calculation and its result on your graph for " q_{soln} vs moles" for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, clearly labeling all of the values.)

