Solution Calorimetry with Electrical Heating Calibration:  
Hess’s Law and Hydration Energy

OBJECTIVE
The objective of this experiment is to determine the hydration energy a salt using solution calorimeter and Hess’s Law.

INTRODUCTION

Hess’s Law and Hydration Energy

The enthalpy of reaction is defined as the heat gained or lost by a chemical system at constant pressure as a reaction proceeds from reactants to products. It is often given as part of a thermochemical equation, such as that shown for the combustion of hydrogen gas:

\[ H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ} \]

The negative sign indicates that the chemicals lose thermal energy to the surroundings in the reaction. Thus when one mole of hydrogen combines with one-half mole of oxygen to make one mole of water, 286 kJ of energy is released to the surroundings. This is an example of an exothermic reaction. Conditions of constant pressure are achieved by carrying out the reaction in a calorimeter that is open to the constant applied pressure of the atmosphere.

The Hess’s law states that the total enthalpy change during the complete course of a reaction is the same whether the reaction is made in one step or in several steps. We will use the Hess’s law to determine the hydration energy, the enthalpy change for the hydration of an anhydrous compound, such as MgSO₄ and CuSO₄.

\[ MgSO_4(s) + H_2O \text{ (solvent)} \xrightarrow{\Delta H_1} Mg^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)} \]

\[ MgSO_4 \cdot 7H_2O(s) \]

\[ CuSO_4(s) + H_2O \text{ (solvent)} \xrightarrow{\Delta H_1} Cu^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)} \]

\[ CuSO_4 \cdot 5H_2O(s) \]

Based on the above diagram, if one knows the solvation enthalpy of the anhydrous form (MgSO₄ or CuSO₄) \( \Delta H_1 \) and the hydrate form (\( MgSO_4 \cdot 7H_2O \) or \( CuSO_4 \cdot 5H_2O \)) \( \Delta H_3 \), one can determine the hydration energy \( \Delta H_2 \) using

\[ \Delta H_2 = \Delta H_1 - \Delta H_3 \quad \text{(eq 1)} \]
Solution Calorimetry

A solution calorimeter is a device for measuring heats of reactions that occur in solution. For aqueous solutions, an insulated cup can work well. One carries out the reaction in the cup and measures the temperature change (ΔT) over the course of the reaction. Assuming adiabatic conditions – that is, all of the enthalpy of reaction is confined to the insulated cup and its contents with no heat leak to the outside of the cup.

By the calorimeter, the resulting temperature difference ΔT is given as the difference between temperatures corresponding to final and initial state, respectively. Determination of this value would be simple in the case of ideal adiabatic calorimeter. Nevertheless, in the real study there it is not possible to reach zero heat flux between calorimeter and surrounding environment. For example, heat insulation is never ideal and the stirrer supplies mechanical energy that is transformed into heat. Hence, today, we will use a solution calorimeter with the calibration using an electric heater.

Using electric heater in a solution calorimeter

The amount of heat that is absorbed or liberated in a physical or chemical change can be measured in a well-insulated vessel called a calorimeter. You will use a simple calorimeter, Fig. 1, that is suitable for measuring heat changes in solution. Calorimetry is based on the principle that the observed temperature change which results from a chemical reaction can be simulated with an electrical heater. The electrical measurements of current (I), heater resistance (R), and duration (t) of heating make it possible to calculate the amount of heat equivalent to that which was produced by the chemical change; the formula $I^2Rt$ is used, as derived in the following paragraph. The use of weighed quantities of reactants makes it possible to calculate the heat change per gram.

Electrical Energy

Electrical current, measured in amperes, is the time rate of flow of electrical charge (coulombs); by definition,

$$\text{amperes} = \frac{\text{coulombs}}{\text{seconds}}$$

The common relationships between electrical potential in volts (V), current in amperes (I), and resistance in ohms (R) is known as Ohm’s Law,

$$V = IR$$

Electrical energy is given by

$$\text{Energy} = (\text{volts})(\text{amperes})(\text{seconds}) = (\text{volts})\left(\frac{\text{coulombs}}{\text{seconds}}\right)(\text{seconds})$$

$$E = I^2 \text{Rt \ volt \ coulombs}$$
By definition:
1 joule = 1 volt coulomb

By combining these laws and definitions, we get
Electrical energy = I^2 R t joules

Figure 1. Calorimeter and power supply.

The Calorimeter
The calorimeter operation is outlined below with reference to Fig. 1. The 200-ml Al cup is surrounded by Styrofoam insulation to minimize heat loss or gain through the walls. The transparent Lucite cover (C) serves as a support for the electrical immersion heater (H); it also has two holes, one which permits the insertion of the thermometer probe (T) and one which provides an opening for the purpose of adding reactants. The solution is stirred by means of a Teflon-covered magnet (M) which is rotated by means of the motor-driven magnet (M').

The temperature is measured by means of a semiconductor junction which is located at the end of the thermometer probe. When a constant current is passed through the junction a voltage is developed which is directly proportional to the temperature of the junction. The voltage is measured with a digital voltmeter. The junction will determine temperature changes to a precision of 0.001°C. The actual temperature can be obtained to an accuracy 0.1°C by adding 10.0 to the reading of the digital voltmeter.

Figure 1 shows a greatly simplified circuit that indicates how the electrical heating is measured and controlled. The double-pole switch (S) controls two things simultaneously: the timer (W), and the constant current source, represented by the battery (B) and the resistance (Z), that supplies the current that flows through the heater (H). The current (I) which flows through the heater is read from the ammeter (A). The resistance of Z is chosen so as to give a current of about 1 ampere through the circuit. The heater resistance has already been measured on another instrument and its value will be shown on a label at your calorimeter. The timer will give you, to the nearest 0.1 sec, the length of time that the current passes through the heater. You will take
temperature measurements at 30-sec intervals before, during, and after the electrical heating process, and for this purpose you will use the ordinary wall clock.

Treatment of the Data

Experimentally, it is almost impossible to exactly duplicate the temperature change due to a chemical reaction by electrical heating. Instead, it is customary to calibrate the calorimeter; that is, find the number of joules of electrical energy required to raise the temperature of the reaction mixture and calorimeter by 1.000°C. This calibration is made by dividing the total electrical energy input ($E_C$) by the temperature rise ($\Delta T_C$) resulting from the input, to give the calibration factor $E_C/T_C$, joules per degree. Then, to obtain the energy resulting from the chemical change, all you have to do is multiply this calibration factor by the observed temperature change ($\Delta T_X$) for the reaction.

$$\text{Energy of the Chemical Change} = \left( \frac{E_C}{\Delta T_C} \right) \Delta T_X$$

Because the calorimeter is not perfectly insulated, it slowly loses or gains heat depending on whether it is warmer or cooler than its surroundings. An accurate determination of the temperature changes for both the reaction and the heater requires that some allowance be made for this slow rate of cooling or heating that occurs in the calorimeter when it is not in use. Therefore, before mixing the reactants (or turning on the heater) a continuous record is made for several minutes of the very slow rate of temperature change while the calorimeter liquid is being stirred; then, after mixing the reactants (or turning off the heater) another record is kept for several minutes of the very slow rate of temperature change of the reaction mixture.

A plot of typical data for a complete heat of solution and calibration experiment is shown in Fig. 2. The linear sections of the plot before and after the major temperature changes are extrapolated forward and backward in time. One vertical line is drawn at a time corresponding to 15 sec after the addition of the salt, and another at the midpoint of the time interval between turning the heater on and 30 sec after turning the heater off. $\Delta T_X$ is then taken as the vertical distance between the points at which the first vertical line intersects the lines extrapolated before and after adding the salt; $\Delta T_C$ is taken as the vertical distance between the points at which the second vertical line intersects the lines extrapolated before and after using the heater. Since $\Delta T_X$ and $\Delta T_C$ should be estimated to the nearest 0.001°C, the graph must be carefully plotted on a generously large scale.
Figure 2. Plot of sample data for a heat-of-solution and calibration experiment

Note that in order to obtain the data for the graph just described it is necessary to record the temperature as a function of actual time as measured on the wall clock. In addition, in order to calculate the electrical energy dissipated in the calibration of the calorimeter, the length of time during which the current flows must be obtained independently from the calorimeter timer.

APPARATUS AND MATERIALS

1. DC power supplier with an ammeter
2. A Vernier device with Thermometer probe
3. A stop watch
EXPERIMENTAL PROCEDURE

1. **Weighing the Salt Sample and Solvent Water**
   (a) Obtain the salt sample in anhydrous form (MgSO₄ or CuSO₄) from the desiccator and transfer it to your desiccator. Record the number of the sample in your notebook.
   (b) Put a weighing boat on the analytical balance and tare the balance to zero; then accurately weigh approximately 2.0-2.5 g of your dried salt in the boat. Put the weighing boat containing the sample into a second desiccator for transport to your calorimeter.
   (c) Put a magnetic stirring bar into the dry Al-cup of the calorimeter.
   (d) Add approximately 150 ml distilled water to the Al-cup using your 150-ml volumetric flask.

2. **Preparing the Apparatus for Measurements**
   (a) Place the Lucite cover with the thermometer probe in place over the cavity of the Styrofoam block on the magnetic stirrer. Turn on the digital thermometer (i.e., the Vernier) and note the room temperature reading. Remove the cover, place the Al-cup into the cavity, and put the Lucite cover on the cup. Turn on the magnetic stirrer so as to give vigorous stirring.
   (b) Turn on the power supply. The power on pilot light must light.
   (c) If the temperature of the water does not lie about 0.3-0.5° above the room temperature reading of your digital thermometer, turn the switch of the heating circuit ON and heat the water until the temperature does lie in this range; then turn the heating circuit switch OFF. Press the reset button beside the dial of the timer.

3. **Establishing the Initial Temperature**
   Commence a 15-20 minute series of temperature measurements taken in unbroken succession (through step 6 below) at 30-sec intervals; use the wall clock for determining the 30-sec intervals when the digital thermometer is read.

4. **Introducing the Salt Sample**
   When it is clear from the measurements of about the first 5 minutes that the temperature is changing only slowly and in a regular manner, prepare for the addition of the salt sample as follows. Immediately following one of the 30-sec temperature observations:
   (a) Remove the weighed salt sample from the desiccator.
   (b) Insert the dry powder funnel into the larger hole at the front of the Lucite cover. Do not insert the funnel prior to this in order to avoid the possibility of moistening the funnel with spray generated by stirring.
   (c) Poise the salt sample over the funnel with one hand and hold the brush in the other hand.
   (d) At the time normally scheduled for making the next 30-sec temperature observation, pour
the salt sample into the tunnel brushing any remaining salt from the boat and funnel into the beaker. Do not try to read the temperature of the solution at the instant you add the sample; merely record which of the 30-sec points was used for addition to the sample.

(e) Check to make sure that the magnetic stirrer is spinning. If it is not, turn down the speed control until it begins spinning again and then readjust the speed to give vigorous stirring.

5. **Re-establishing a Steady-State Temperature**
   Again read the temperature at 30-sec intervals, even though the first reading after adding the salt is not a very stable one. Continue taking measurements until the temperature has been relatively stable (or slowly changing in a regular manner) for about 5 minutes after adding the salt.

6. **Calibration of the Calorimeter**
   When the temperature baseline has been established, take a thermometer reading at a regular 30-sec interval and simultaneously close the switch of the heating circuit. Let the current flow until the solution temperature approximates what it was before you added the salt, then turn the heater OFF. During the heating period continue to take temperature measurements at the scheduled 30-sec intervals but realize that they can be only approximate, since the temperature will be changing rather rapidly. Also during the heating period while the current is flowing, tap the ammeter gently and record the ammeter reading to the nearest 0.001 amp.

   After turning off the heater, continue to record the temperature at 30-sec intervals for a period of 3-5 minutes after the temperature stops rising. Record, to the nearest 0.1 sec, the reading on the timer. Record the resistance of the heater used in your calorimeter; it is given on a label on the calorimeter.

7. **Repeating the Determination**
   (a) Remove the Al-cup from the Styrofoam block. Remove the Lucite cover and gently wipe the heater and thermometer probe with a tissue. Put the cover over the cavity. Empty the Al-cup, being careful not to lose the stirring bar. Rinse the Al-cup and stirring bar and wipe dry with a Kimwipe.
   (b) Repeat the entire experiment twice more for each sample, starting each time with the dry Al-cup.
   (c) When you are finished turn off the power supply and the digital thermometer.

8. **Repeating the above procedure (1-7), and measuring the solvation enthalpy for the hydrate salt** $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

**Data Analysis (to be included in your full report)**
*You can the following data sheet for your convenience of recording the data. You need to include the data here as tables in your full report.*

1. Plot your measurements of temperature vs. time for both the calibration and the solution of the anhydrous salt and the hydrate salt, respectively.
2. Calculate the enthalpy of solution per gram of solute for each run, the mean value, the
standard deviation, and the relative 95% confidence interval of the mean expressed as parts per hundred (%)
3. Please report the heat capacity in $J \cdot ^\circ C^{-1}$ for your calorimeter, using $C=\frac{q}{\Delta T}$.
4. Calculate the hydration energy for MgSO$_4$ or CuSO$_4$? How much different are your data from the literature values? Please analyze what are the potential sources of errors for causing the difference. Note that you need to rationalize why your identified sources of errors can lead to the overestimation or underestimation of the measured hydration energy.
5. Compared the solvation enthalpies for the anhydrous and the hydrate salts, and explain (e.g., from the molecular viewpoint) why one is larger than another in magnitudes.
# Data Sheet for Solution Calorimetry with Electric Heating Calibration: Hess’s Law and Hydration Energy

**NAME** _______________________________ **Lab Section** ___________

**Date Report Submitted** ______________________

## 1. Enthalpy of Anhydrous Salt

<table>
<thead>
<tr>
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<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
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<tbody>
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<td>Weight of salt (g)</td>
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<td>Weight of water (g)</td>
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<td>Solution concentration</td>
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<td>(g/kg of water)</td>
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<td>$\Delta T_x$ caused by solution of salt</td>
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<td>(from graph)</td>
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<td>$\Delta T_C$ caused by electrical heating</td>
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<td>(from graph)</td>
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<td>Ammeter reading (amp)</td>
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<td>t, time during which current passed (sec)</td>
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<td>$E_C$, electrical energy input</td>
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<td>Calibration factor ($E_C/\Delta T_C$)</td>
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<tr>
<td>Enthalpy of solution (J/g)</td>
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Average enthalpy of solution (J/g)___________
Standard deviation_________________________
Relative 95% confidence interval of the mean, %___________
2. Enthalpy of the Hydrate Salt

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<td>Calibration factor ($E_C/\Delta T_C$)</td>
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<td>Enthalpy of solution (J/g)</td>
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|                          |          |          |          |
| Average enthalpy of solution (J/g) |          |          |          |
| Standard deviation |          |          |          |
| Relative 95% confidence interval of the mean, % |          |          |          |