12. BUILDING A BETTER HAND WARMER

Introduction

If you have ever attended a football game in Denver, CO or Buffalo, NY in the middle of winter, there is a good chance you are familiar with flameless chemical hand warmers that keep your fingers from freezing in the cold. Likewise, if you suffer a sprain while playing football, your coach will have used an instant cold pack to stem swelling. Such commercial products take advantage of the energy changes that accompany the physical and chemical transformation of matter. Fundamental to these commercial applications is calorimetry, the science of heat transfer. In this lab, you will use calorimetry to investigate the heat of solution of common ionic compounds and your results will be used to design a hand warmer that is safe, effective and inexpensive.

Concepts

- Enthalpy
- Calorimetry
- Specific heat
- Heat of solution
- Exothermic reactions
- Endothermic reactions
- System and surroundings

Background

Most commercial hand warmers are small packets containing an ionic salt and water contained in separate compartments. Heat is generated when the physical barrier between water and solid is broken and dissolution of the solid produces a large temperature change.

Thermochemistry is the study of the energy that is lost or gained in a chemical reaction. *Enthalpy* is a thermodynamic quantity that is equivalent to the total heat content of a chemical system. The energy or enthalpy change associated with the process of a solute dissolving in a solvent is called the heat of solution ($\triangle$Hsoln). At constant pressure, this enthalpy change is equal to the amount of heat loss or gain (q) to the surroundings. Although the amount of enthalpy cannot be measured directly, scientists can determine how much it changes. When an ionic solid dissolves in water, three processes govern the overall change in energy: (1) the energy required to break ionic attractions within the crystal lattice of the solid, (2) energy required to break hydrogen bonding forces between water molecules and (3) energy released when dissociated ions form ion-dipole associations with water molecules. If the amount of energy released in the formation of ion-dipole associations is greater than the energy required to separate the solute and solvent particles, then the net energy change is negative and the process of dissolution releases heat or is exothermic. If the amount of heat energy released in the formation of ion-dipole associations during dissolution is less the amount of energy required to separate particles of solute and solvent from each other, the net sum of energy changes will be positive and the process absorbs heat or is endothermic.

In order to measure enthalpy changes, experiments must be conducted in an insulated reaction vessel known as a calorimeter. The design of a calorimeter minimizes heat loss to the environment outside of the reaction vessel. In the ideal scenario, heat exchange only occurs between a dissolving solid and the solvent it is placed in (system). However, calorimetric measurements must always account for any heat exchange, however minimal, between the instrument and the environment (surroundings).

When using a calorimeter, solute and solvent are mixed in the reaction vessel and temperature recorded at the start and at the end of the reaction. If a reaction releases heat, an exothermic reaction, then the temperature of the water will increase. On the other hand, an endothermic reaction will absorb heat from the water, thus causing a decrease in the temperature of the water. This allows for a simple calculation of the heat of the reaction by first measuring the temperature change for the water, and then using the following equation to calculate the heat q absorbed our released by the dilute solution:

$$q = mc\Delta T$$

where m is the mass of the solution, solute plus solvent, (assume the mass of 1.00 mL of solution is 1.00 g), c is the specific heat capacity of water: 4.184 J/g°C, and $\Delta T = T_{\text{final}} - T_{\text{initial}}$ of the solution. When the solutions used are dilute, they are assumed to have the same thermal properties as water.

When measuring the total heat of solution for an exothermic reaction using a calorimeter, the heat released during the solute dissolution process is absorbed by the solvent (qaq) plus a small amount of heat absorbed by the calorimeter itself (qcal). The equation for overall heat transfer is:

$$\text{qsoln} = -(\text{qaq} + \text{qcal})$$

The heat capacity of the calorimeter (qcal), sometimes referred to as the calorimeter constant, must be taken into account. The units for this value are in J/oC. The calibration requires mixing equal volumes of hot and cool water in the calorimeter. The temperature of the mixture is measured after 20 seconds (Tmix). Additionally, the average temperature (Tavg) of the hot (Th) and cool (Tc) is also calculated using the following equation:

$$(\text{Tavg}) = (\text{Th} + \text{Tc})/2$$

The difference between Tavg and Tmix represents the heat lost by water to the calorimeter. This value must be included in the calculation for qwater:

$$\text{qwater} = (\text{mass of water}) \times (\text{specific heat of water}) \times (\text{Tmix} - \text{Tavg})$$

Thus, the heat gained by the calorimeter, qcalor, is equal to the heat lost by water but with an opposite sign. The calorimeter constant, Ccal, equation is:

$$\text{Ccal} = \text{qcalor} / (\text{Tmix} - \text{Tinitial})$$

where Tinitial is the initial temperature of the calorimeter containing cool water. Thus, in order to determine the heat of solution or heat of reaction for any system using the equation

$$\text{qsoln} = -(\text{qaq} + \text{qcal})$$

the correction value qcal must be calculated by multiplying the calorimeter constant (Ccal) by the change in temperature of that solution (△T):

$$\text{qcal} = \triangle\text{T (oC)} \times \text{Ccal (J/oC)}$$

This investigation begins with determination of the heat capacity of the calorimeter. The capacity of a calorimeter to minimize the value for qcal varies depending on the calorimeter itself. For the purpose of this investigation, the use of a calorimeter (PASCO TD-8825A) is recommended. Alternatively, you may conduct the experiment using two nested Styrofoam cups and a corrugated cardboard cover with a hole punctured to fit a wireless temperature sensor. For the Initial Investigation, the heat capacity of the calorimeter as well as the heat transfer from the dissolution of a model ionic salt, magnesium sulfate ($MgSO_4$) will be determined. For the Advanced Investigation, the heat energy transfer of a number of ionic salts will be determined. The selection of the best hand warming compound will be made based on values for heat transfer measured against materials cost and safety (toxicity).

Pre-Lab Questions

1. When magnesium chloride, $MgCl_2$, dissolves in water, the temperature of the water increases.

   a. (True or False): The heat of solution is endothermic.

   b. Are the intramolecular forces between water molecules and between magnesium and chloride ions stronger or weaker than the combined intermolecular forces between water molecules and ionic bond strength of $MgCl_2$? Explain.

   c. Calculate the amount of heat energy released, q_{soln} , when 20.0 g of an ionic salt is added to 60.0 mL of distilled water with an initial temperature of 22.1 °C. The final temperature is measured at 26.5 °C. Assume no heat loss to the calorimeter.

Materials and Equipment

Use the following materials to complete the initial investigation. For conducting an experiment of your own design, check with your teacher to see what materials and equipment are available.

- Data collection system
- Wireless temperature sensor
- Calorimeter (TD-8825A)
- 100-mL graduated cylinder
- Electronic balance, 0.01-g precision
- Heat-resistant gloves
- Support stand and ring clamp
- Magnetic stirrer and stir bar
- Weighing boats
- Ammonium chloride (NH_4Cl), 15 g
- Calcium chloride ($CaCl_2$), 15 g
- Lithium chloride (LiCl), 15 g
- Sodium carbonate (Na_2CO_3), 15 g
- Magnesium sulfate ($MgSO_4$), 15 g
- Sodium acetate ($NaCH_3COO$), 15 g
- Stopwatch

Safety

Follow these important safety precautions in addition to your regular classroom procedures:

- Wear safety goggles at all times
- Lithium chloride is moderately toxic by ingestion.
- Magnesium sulfate may irritate body tissues.
- Sodium acetate is a respiratory tract and body tissue irritant.
- Calcium chloride and ammonium chloride are mildly toxic by ingestion.
- Avoid contact of chemicals with eyes and skin.
- Wash hands thoroughly with soap and water before leaving laboratory.
- Dispose of solutions as directed by Material Safety Data Sheets.
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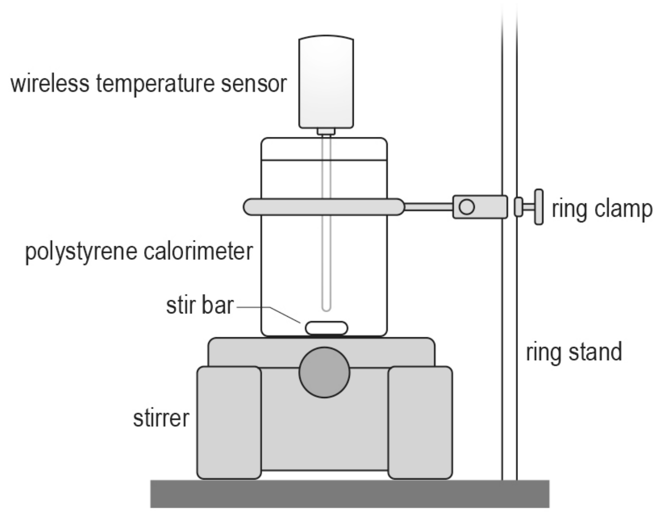
Initial Investigation

Heat capacity of the calorimeter

1. Start a new experiment on the data collection system from your Chromebook, computer or mobile device.
2. Connect the wireless temperature sensor to the data collection system.
3. Set up a calorimeter using a ring clamp and attach to a support stand.
4. Lower the calorimeter onto a magnetic stirrer and place a stir bar inside the calorimeter.
5. Measure 100.0 mL of distilled water into the calorimeter.
6. Turn on magnetic stirrer and set the bar spinning slowly.
7. Measure and record the initial temperature of the water.
8. Heat 120.0 mL of distilled water in a 250-mL beaker to 60-70 °C.
9. Measure 100.0 mL of the hot water in a 100 mL graduated cylinder.



10. Measure and record initial temperature of hot water.
11. Add hot water to room temperature water in calorimeter.
12. Replace calorimeter cover and immediately insert temperature sensor.
13. Measure and record temperature (T_{mix}) at 20-second mark.
14. Empty and dry calorimeter to prep for the next activity.
15. Calculate the calorimeter constant (C_{cal}) using T_{mix} and equations from the *Background* section of this lab.

Volume of deionized water, cold	
Temperature, cold water ($T_{initial}$)	
Volume of deionized water, hot	
Temperature, hot water	
Final temperature (T_{mix})	
Net temperature change, cold water	
Net temperature change, hot water	
Enthalpy change, cold water, q_{cold} (J)	
Enthalpy change, hot water, q_{hot} (J)	
Temperature change, calorimeter	

Enthalpy change, calorimeter, q_{cal} (J)	
Calorimeter constant, (J/°C)	

Calorimetry with magnesium sulfate

1. Measure 100.0 mL of distilled water and transfer into calorimeter.

2. Measure and record initial temperature of water.

3. Weigh out 5.00 g of magnesium sulfate ($MgSO_4$) in a clean weigh boat.

4. Place a clean magnetic stir bar into the calorimeter and begin stirring slowly.

5. Add all of the magnesium sulfate to the calorimeter and immediately insert temperature sensor into the solution.

6. Measure and record the lowest and highest temperatures of the dissolution process.

7. Calculate the molar heat of solution for magnesium sulfate with correction due to heat lost to the calorimeter.

Volume of deionized water	
Density of water	
Mass of water	
Mass of magnesium sulfate ($MgSO_4$)	
Initial temperature	
Final temperature	
Temperature change	

Advanced Investigation

1. Review the calorimetry procedure from the Initial Investigation and equations in Background to calculate the enthalpy change for a reaction.

2. Select three solids from the Ionic Solids list.

3. Design and implement experiments to determine the heat of solution for each solid paying special attention to safety and handling instructions for each substance.

4. Using cost data from the Ionic Solids list, use collected calorimetry data to extrapolate which substance(s) could be used to produce an effective hand warmer. Use the following guidelines in your analysis.

   a. The hand warmer must contain 10.0 g of the solid to be mixed with 40.0 mL of water.

   b. A minimum 20°C temperature increase from the dissolution process upon activation is required.

   c. The ionic solid must be inexpensive, safe and nontoxic to humans and the environment.

Note: Review the Material Safety Data Sheet for each proposed substance.

Ionic Substance	Formula Mass (g/mol)	Cost (US$/500 g)
Ammonium chloride (NH_4Cl)	53.49	12.20
Calcium chloride ($CaCl_2$)	110.98	7.75
Lithium chloride (LiCl)	42.39	35.75
Sodium acetate ($NaCH_3COO$)	82.03	14.15
Sodium carbonate (Na_2CO_3)	105.99	10.90
Sodium chloride (NaCl)	58.44	7.35

Sodium Chloride (NaCl)

Volume of deionized water	
Mass of NaCl	
Initial temperature	
Final temperature	
Temperature change	

Sodium Acetate ($NaCH_3COO$)

Volume of deionized water	
Mass of $NaCH_3COO$	
Initial temperature	
Final temperature	
Temperature change	

Lithium Chloride (LiCl)

Volume of deionized water	
Mass of LiCl	
Initial temperature	
Final temperature	
Temperature change	

Calcium Chloride ($CaCl_2$)

Volume of deionized water	
Mass of $CaCl_2$	
Initial temperature	
Final temperature	
Temperature change	

Sodium Carbonate (Na_2CO_3)

Volume of deionized water	
Mass of Na_2CO_3	
Initial temperature	
Final temperature	
Temperature change	

Ammonium Chloride (NH_4Cl)

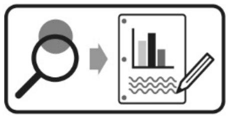
Volume of deionized water	
Mass of NH_4Cl	
Initial temperature	
Final temperature	
Temperature change	

Solid	Temperature Change, ΔT, (°C)	Energy Change: Calorimeter contents, q_{aq} (J)	Energy change: Calorimeter, q_{cal} (J)	Internal energy change, q_{soln} (J)	Enthalpy of dissolution, ΔH_{soln} (kJ/mol)
NaCl					
$CaCl_2$					
$NaCH_3COO$					
Na_2CO_3					
LiCl					
NH_4Cl					

5. Given the cost information detailed above and information from the MSDS sheet for each potential hand warmer, determine which of the compounds studied best falls within the size, cost and safety guidelines specified in this study.

Solid	**Cost (USD/g)**	**$\triangle$T (°C) 50.0 mL**	**$\triangle$T (°C) 40.0 mL**	**Extrapolated $\triangle$T 10 g/40 mL**	**Total Cost of Solid per 10-g Unit**
$NaCl$					
$CaCl_2$					
$NaCH_3COO$					
Na_2CO_3					
$LiCl$					
NH_4Cl					

Extended Inquiry Investigation



Instant cold compress

Design a protocol to develop a safe and inexpensive cold compress for use in first aid. The product must contain 10 g of ionic salt and 20 mL water. Using online sources, prepare a list of ionic compounds whose dissolution in water is endothermic. Research their safety using Material Safety Data Sheets. Use compound pricing to determine which compound combination is the most ideal to use in producing the cold compress.

Synthesis Questions

1. Hess's Law:

   a. Gives the heat of reaction for a reaction obtained by combining the heat of reaction of other reactions.
   b. Provides evidence that the heat of reaction is independent of the path of the reaction.
   c. Can be used to obtain the heat of reaction for reactions not possible to perform.
   d. All of the above.

2. The heat capacity of the calorimeter is:

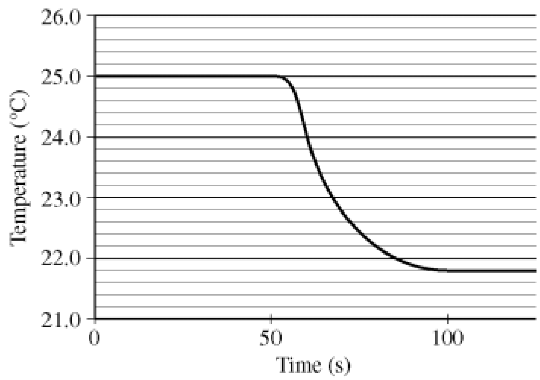
   a. The amount of heat necessary to increase the temperature of the calorimeter, including the solutions,1°C.
   b. The same as the heat of reaction per mole of reactant.
   c. Can be obtained from the heat of reaction of the combined reactions.
   d. Is usually negligible.

3. The heat change that accompanies the dissolution processes can be measured with calorimetry as well. In an experiment, 5.00 g of NH_4NO_3 was dissolved in 50 mL of water in a polystyrene cup calorimeter. The temperature dropped from 23.50°C to 17.57°C. What is the heat of reaction for the dissolution of NH_4NO_3?

   a. $\triangle H = +\ 1330$ J/mol.
   b. $\triangle H = +\ 21.3$ kJ/mol.
   c. $\triangle H = -\ 21.3$ kJ/mol.
   d. $\triangle H = +\ 2130$ J/mol.

AP® Chemistry Review Questions

A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2. The student places 91.95 g of water at 25°C into a coffee cup calorimeter and immerses a thermometer in the water. After 50 seconds, the student adds 5.13 g of solid urea, also at 25°C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.



a. Determine the change in temperature of the solution that results from the dissolution of the urea.

b. According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

c. Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J/g °C throughout the experiment.

(i) Calculate the heat of dissolution of the urea in joules.

(ii) Calculate the molar enthalpy of solution, $\triangle H^{\circ}_{soln}$ of urea in kJ/mol.

(iii) Using the information in the table below, calculate the value of the molar entropy of solution, $\triangle S^{\circ}_{soln}$, of urea at 298 K. Include units with your answer.

	Accepted Value
$\triangle H^{\circ}_{soln}$ of urea	14.0 kJ/mol
$\triangle G^{\circ}_{soln}$ of urea	-6.9 kJ/mol