

Heats of Transition, Heats of Reaction, Specific Heats, and Hess's Law

GOAL AND OVERVIEW

A simple calorimeter will be made and calibrated. It will be used to determine the heat of fusion of ice, the specific heat of metals, and the heat of several chemical reactions. These heats of reaction will be used with Hess's law to determine another desired heat of reaction.

Objectives and Science Skills

- Understand, explain, and apply the concepts and uses of calorimetry.
- Describe heat transfer processes quantitatively and qualitatively, including those related to heat capacity (including standard and molar), heat (enthalpy) of fusion, and heats (enthalpies) of chemical reactions.
- Apply Hess's law using experimental data to determine an unknown heat (enthalpy) of reaction.
- Quantitatively and qualitatively compare experimental results with theoretical values.
- Identify and discuss factors or effects that may contribute to deviations between theoretical and experimental results and formulate optimization strategies.

SUGGESTED REVIEW AND EXTERNAL READING

- See reference section; textbook information on calorimetry and thermochemistry

BACKGROUND

The internal energy, E , of a system is not always a convenient property to work with when studying processes occurring at constant pressure. This would include many biological processes and chemical reactions done in lab. A more convenient property is the sum of the internal energy and pressure-volume work ($-w_{\text{sys}} = P\Delta V$ at constant P). This is called the *enthalpy* of the system and is given the symbol H .

$$H \equiv E + pV \quad (\text{definition of enthalpy, } H) \quad (1)$$

Enthalpy is simply a corrected energy that reflects the change in energy of the system while it is allowed to expand or contract against a constant pressure. For any process occurring at constant pressure, the *change in the enthalpy*, ΔH , is the *heat absorbed or released* by the system.

$$\Delta H \equiv H_{\text{final}} - H_{\text{initial}} = q_p = \text{heat absorbed by system} \quad (\text{constant } p) \quad (2)$$

A system can be thought to “contain” enthalpy, just as it does energy. Some contributions to the enthalpy of a system include the following.

- 1 Thermal Enthalpy. The *higher* the system’s *temperature*, the greater its *enthalpy*. This makes sense because it takes *heat* to *raise* the *temperature* of an object.
- 2 Phase Enthalpy. The *liquid* phase has *higher enthalpy* than the *solid*, and the *vapor* phase has higher enthalpy than the *liquid*. This also makes sense because it takes heat to melt a solid or to vaporize a liquid.
- 3 Chemical Enthalpy. Chemical bonds store energy. When a chemical reaction occurs, the chemical enthalpy of the reactants changes when they form products.
 - i If the reaction is *exothermic*, the *chemical enthalpy decreases* as the reaction proceeds.
 - ii If the reaction is *endothermic*, the *chemical enthalpy increases* as the reaction proceeds.

Enthalpy changes are determined by measuring the amount of heat transferred during a physical or chemical process. The quantitative treatment of the above three kinds of enthalpy, are all based on use of Eq. 2.

Temperature

When there is a change in the temperature of the system, ΔH is proportional to the temperature change, $T_{\text{final}} - T_{\text{initial}} = \Delta T$. The proportionality constant is called the **heat capacity**, and is given the symbol C .

$$\Delta H \equiv H_{\text{final}} - H_{\text{initial}} = C(T_{\text{final}} - T_{\text{initial}}) = C\Delta T \quad (\text{temperature change}) \quad (3)$$

Because it is the difference in temperature that determines ΔH , either °C or K temperatures will give the identical result.

ΔH of the system is also proportional to the *amount of material*. The heat energy required to raise the temperature of one gram of material is its specific heat capacity, c . If amount is expressed in moles, then the molar heat capacity C is used.

$$C_{\text{total}} \equiv m c_{\text{per gram}} = n C_{\text{per mole}} \quad (4a)$$

Therefore, the system’s ΔH is the product of the amount, the heat capacity (specific or molar), and the change in temperature.

$$\Delta H = C_{\text{total}}\Delta T = m c_{\text{per gram}}\Delta T = n C_{\text{per mole}}\Delta T \quad (4b)$$

If ΔT of the system is positive, temperature increases, the system absorbs heat, and q (or ΔH) is positive. If ΔT of the system is negative, temperature decreases, the system gives off heat to its surroundings, and q (or ΔH) is negative.

Unit analysis will help you determine how to use the above equation. ΔH (or q) must have an energy unit. Units for heat capacity are:

c :	energy per gram per degree	e.g., $\text{J}/^\circ\text{C} \cdot \text{g}$
C :	energy per mole per degree	e.g., $\text{J}/^\circ\text{C} \cdot \text{mol}$
C_{general}	energy per degree	e.g., $\text{J}/^\circ\text{C}$.

Phase

At a phase change, the temperature of the system is constant until the transition is complete. The amount of heat required is proportional to the amount of material present, and the ΔH of the phase transition. The heat energy can also be expressed in terms of moles (heat per mole).

$$\Delta H = m \Delta h_{\text{per gram}} = n \Delta H_{\text{per mole}} \quad (\text{phase change}) \quad (5)$$

The value of ΔH is positive (heat is absorbed) for melting, vaporization, and sublimation processes. It is negative for the reverse (freezing, condensation, and deposition). In this experiment, we will use ' Δh ' to represent the enthalpy change per gram.

Chemical Reaction

The chemical reactions studied here occur at a particular pressure and temperature. Each reaction has an associated enthalpy change that is called the heat or enthalpy of reaction that depends on the way the reaction is balanced. For example, $\Delta H_{\text{reaction}}$ for $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$ is twice that for $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$, and $\Delta H_{\text{reaction}}$ is the heat absorbed when 2 moles of water decompose to give two moles of hydrogen and one mole of oxygen. In general, the equation to calculate the heat change is similar to Eq. 5.

$$\Delta H = m \Delta h_{\text{per gram}} = n \Delta H_{\text{per mole}} \quad (\text{reaction}) \quad (6)$$

Calorimeter

A calorimeter is an insulated vessel in which physical or chemical processes are performed while neglecting heat flow between the vessel and its surroundings. A process in which the heat flow, q , equals zero is called *adiabatic*.

To a first approximation, the heat flow (+ or -) between calorimeter and the surroundings is zero, so ΔH (or q) for the calorimeter and its contents will be zero.

$$\Delta H_{\text{calorimeter and contents}} = q_{\text{total}} = 0 \quad (\text{master equation for calorimeters}) \quad (7)$$

Example 1: Calorimeter Calibration

A mass m_1 of water at temperature T_1 is placed in the calorimeter. Mass m_2 of water at T_2

is added. The calorimeter itself has a small heat capacity that must be accounted for in order to have reasonable precision. The calorimeter always contributes a term to the total enthalpy change.

$$\Delta H_{\text{calorimeter}} = C_{\text{calorimeter}}(T_{\text{final}} - T_{\text{initial contents}}) \quad (8)$$

Initially, the calorimeter is at the same temperature, T_1 , as the water it contains. When heat flow stops, all of the water and the calorimeter have reached the same temperature T_{final} (at thermal equilibrium). In this example, there are three quantities contributing to the total enthalpy change (which is assumed to be zero): the two amounts of water and the calorimeter.

$$\Delta H_{\text{total}} = 0 \quad (9a)$$

$$\Delta H_1 + \Delta H_{\text{calorimeter}} + \Delta H_2 = 0 \quad (9b)$$

$$m_1 c_{\text{water}}(T_{\text{final}} - T_1) + C_{\text{calorimeter}}(T_{\text{final}} - T_1) + m_2 c_{\text{water}}(T_{\text{final}} - T_2) = 0 \quad (9c)$$

Note that the initial temperatures are not the same, but everything shares a common final temperature. Eq. 5 was used for ΔH_1 and ΔH_2 . Generally all but one quantity in calculations like that shown in Eqns 9a, 9b, and 9c are measured or known. The equation is then solved for the unknown value.

Example 2: Specific Heat Determination

Suppose a mass m_1 of water with specific heat c_1 is placed in the calorimeter at T_1 . Then a mass m_2 of another substance, such as a metal, at T_2 and with specific heat c_2 is added. The equation is similar to that of Eqns 9a, 9b, and 9c except that the ‘c’s do not cancel in the last step.

$$\Delta H_{\text{total}} = 0 \quad (10a)$$

$$\Delta H_1 + \Delta H_{\text{calorimeter}} + \Delta H_2 = 0 \quad (10b)$$

$$m_1 c_{\text{water}}(T_{\text{final}} - T_1) + C_{\text{calorimeter}}(T_{\text{final}} - T_1) + m_2 c_2(T_{\text{final}} - T_2) = 0 \quad (10c)$$

Note again that the initial temperatures are not the same, but everything shares a common final temperature. Eq. 5 was used for ΔH_1 and ΔH_2 . Again, usually all but one quantity are measured or known. The equation is then solved for the unknown value.

In 1819, after analyzing the heat capacities of many solid elements, Dulong and Petit proposed this generalization known as the *Law of Dulong and Petit*:

$$C_{\text{per mole}} = MM c_{\text{per gram}} = \text{constant for all metals} = 3R \quad (11)$$

MM = molar mass of the metal; R = gas constant (8.314 J/k · mol).

Using precise specific heat measurements, Berzelius used Eq. 11 to find many molar masses. In 1830, he published an extremely accurate table of molar masses that gave great impetus to the development of atomic/molecular theory.

Example 3: Enthalpy of Phase Change Determination

Suppose a mass m_1 of water is placed in the calorimeter at T_1 , and mass m_2 of ice at 0°C is added. As the apparatus reaches thermal equilibrium, several things occur.

First, the ice melts, pulling its heat of fusion out of the thermal energy of the water and calorimeter, thus lowering their temperatures. Second, when the ice has melted, the resulting liquid is still at 0°C , so that water has to be further heated until it, the water it is cooling, and the calorimeter reach the same final temperature.

$$\Delta H_{\text{total}} = 0 \quad (12a)$$

$$\Delta H_{\text{cool water}} + \Delta H_{\text{cool calorimeter}} + \Delta H_{\text{melt ice}} + \Delta H_{\text{warm melted ice}} = 0 \quad (12b)$$

$$m_1 c_{\text{water}}(T_{\text{final}} - T_1) + C_{\text{calorimeter}}(T_{\text{final}} - T_1) + m_{\text{ice}} \Delta h_{\text{fusion, per g}} + m_{\text{ice}} C_{\text{water}}(T_{\text{final}} - 0^\circ\text{C}) = 0 \quad (12c)$$

Note that the heat of fusion of ice is expressed in units of energy per mass (J/g or kJ/g); if the amount of ice were in moles, the heat of fusion would have units of energy per mole (J/mol or kJ/mol).

Example 4: Reaction Enthalpy Determinations

Suppose mass m_1 of a water-based solution is placed in the calorimeter at T_1 . To that mass m_2 of a substance of molar mass MM_2 is added and it reacts with the solution. If substance 2 is the limiting reactant, then all of it will react. The enthalpy change will depend on the heat of reaction and on the number of moles of substance 2 added, $n_2 = m_2/MM_2$.

In this case, there are three contributions to the total enthalpy change of zero. They are due to the temperature change of the water solution and calorimeter, plus the enthalpy change due to the chemical reaction. For reactions in solution, the heat capacities of the reactants and products are approximated as zero because only the water and the calorimeter have significant heat capacity.

In the last step it is assumed that the chemical reaction is written in such a way that the stoichiometric coefficient on the reactant, substance 2, is 1.

$$\Delta H_{\text{total}} = 0 \quad (13a)$$

$$\Delta H_1 + \Delta H_{\text{calorimeter}} + \Delta H_{\text{chemical reaction}} = 0 \quad (13b)$$

$$m_1 c_{\text{water}}(T_{\text{final}} - T_1) + C_{\text{calorimeter}}(T_{\text{final}} - T_1) + \frac{m_2}{MM_2} \Delta H_{\text{reaction}} = 0 \quad (13c)$$

The last term has been written so that $\Delta H_{\text{reaction}}$ has a unit of energy per mole (J/mol or kJ/mol).

In 1840, Hess stated that the evolution of heat by chemical reactions is the same, regardless of whether the reaction takes place in one step or in more than one. Heats of reaction are changes in the property, H , of a system. When a system changes from state 1 to state 2, H will have to change by the amount $H_2 - H_1$, regardless of the number or kind of steps involved in the process. Hess' Law permits the heats of experimentally difficult reactions to be deduced from measurements of other more convenient reactions.

EXPERIMENTAL NOTES

There are two possibilities for your calorimeter setup, but both require the same procedure.

- Coffee Cup Calorimeter Setup — the calorimeter consists of two nested Styrofoam cups with a lid.
- Styrofoam Calorimeter Setup — the calorimeter consists of a Styrofoam base and lid.

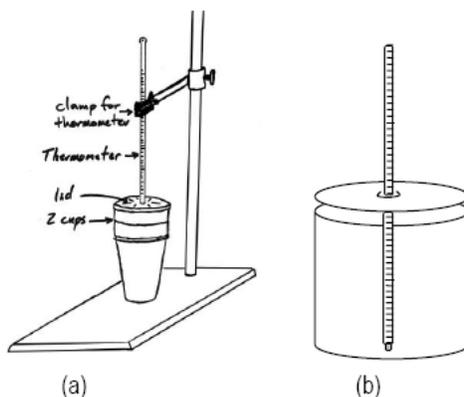


Figure 1

A thermometer is placed through a hole in the lid to measure the temperature of the liquid. If you use set-up (a), use a slotted rubber stopper to protect the thermometer in the clamp. Both setups are constant pressure calorimeters.

Please do not throw your calorimeter away. Return it clean to the reagent bench. this applies to both (a) and (b).

Measurements

The two key measurements for all calorimetry experiments are masses and temperature changes. Make sure you have all of the data you need to complete the lab. You may need these conversion factors: $1000 \text{ J} = 1 \text{ kJ}$, and $4.184 \text{ J} = 1 \text{ cal}$.

Note: Make sure you record/obtain all information required to complete the calculations. This includes the heat capacity of all calorimeters used to gather your data.

PROCEDURE

Part 1: Heat Capacity of the Calorimeter

This is the experiment discussed in Example 1. *This result is important because you will use it in the other experiments you perform with this calorimeter.*

- 1 Record the mass of your calorimeter to 0.01 g.
- 2 Add about 100 mL of room temperature water.
- 3 Record the mass of the calorimeter and water; *determine the mass of this water by difference* to 0.01 g.
- 4 To equilibrate the beaker used to transfer the warm water to the calorimeter, take a small beaker to one of the warm water baths (approximately 35°C) in the lab. Submerge the beaker in the warm water bath for a couple minutes.
- 5 Record the temperature (to the nearest 0.1°C) of the water in both the warm water bath and in your calorimeter just before you add the warm water to the room temperature water.
- 6 Make sure your calorimeter is at least 4 feet away from any hot plate, and try to minimize drafts.
- 7 Using the equilibrated beaker, scoop up about 100 mL of warm water from the water bath and pour it into your calorimeter.
- 8 Quickly put on the lid and insert the thermometer.
- 9 Stir the water and read the final temperature reached by the mixture to 0.1°C.
- 10 Remove the thermometer and record the final mass (so you can determine the mass of warm water added) to 0.01 g.
- 11 **Redo the calibration at least one time** to verify the calorimeter's heat capacity.
- 12 Calculate the heat capacity of your calorimeter, using Eqns. 9a, 9b, and 9c.

$$\Delta H_1 + \Delta H_{\text{calorimeter}} + \Delta H_2 = m_1 c_{\text{water}}(T_{\text{final}} - T_1) + C_{\text{calorimeter}}(T_{\text{final}} - T_1) + m_2 c_2(T_{\text{final}} - T_2) = 0 \quad (9d)$$

Finding the heat capacity of your calorimeter this way is very sensitive to small errors. The "correct" value is probably between 5 and 150 J/°C. If you get a negative value or a very large value, re-do the calculation or the experiment. Use a new set of cups if you get a high calorimeter constant (heat loss).

Part 2: Heat of Fusion of Ice

This is the experiment discussed in Example 3.

- 1 Record the mass of your empty, dry calorimeter to 0.01 g.
- 2 Add about 100 mL of room temperature water.
- 3 Record the mass of the calorimeter and water; *determine the mass of this water by difference* to 0.01 g.
- 4 Place your calorimeter on a ring stand and carefully clamp your thermometer (inserted through a slotted rubber stopper) to the stand so that the thermometer nearly reaches the bottom of the calorimeter.
- 5 Measure the temperature of your water to 0.1°C.
- 6 Add about 25 g of ice. *Solid ice is preferred over slushy ice.* Why is this?
- 7 Swirl the calorimeter to enhance mixing and watch as the temperature falls.
- 8 Record the lowest temperature reached to 0.1°C.
- 9 Carefully remove the thermometer and record the final mass to 0.01 g (so you can determine the mass of ice added).
- 10 Calculate the heat of fusion of ice in J/g, using Eqns. 12a, 12b, and 12c.

$$\begin{aligned} & \Delta H_{\text{cool water}} + \Delta H_{\text{cool calorimeter}} + \\ & \Delta H_{\text{melt ice}} + \Delta H_{\text{warmup melted ice}} = m_1 c_{\text{water}}(T_{\text{final}} - T_1) + \\ & C_{\text{calorimeter}}(T_{\text{final}} - T_1) + m_{\text{ice}} \Delta h_{\text{fusion, per g}} + m_{\text{ice}} c_{\text{water}}(T_{\text{final}} - 0^\circ\text{C}) = 0 \end{aligned} \quad (12d)$$

- 11 Some liquid water probably went into your calorimeter along with the ice. How would that affect your result?
- 12 Convert your answer into units of kJ/mol. Report your answer to three significant figures.
- 13 Calculate the percent error in your experimental result relative to the literature value of 6.01 kJ/mol.

Part 3: Specific Heat of a Metal

Begin the temperature equilibration of the metal at the beginning of the lab.

This is the experiment given in Example 2.

- 1 You will study either copper or aluminum. Record which metal you choose.
- 2 Take 20–30 g of the metal and record the mass to 0.01 g.

- 3 Carefully place the metal in a large test tube suspended in a boiling water bath made in a 400 mL beaker.
- 4 Leave the test tube there for at least 30 minutes to equilibrate the metal to the temperature of the bath. Do this at the start of the experiment so the metal heats while you are doing other things. Keep the calorimeter away from the hot plates.

CAUTION: Steam burns are especially severe, as the steam condenses to liquid on your skin and gives up its heat of vaporization to the tissues. So whenever you work around steam, pay attention.

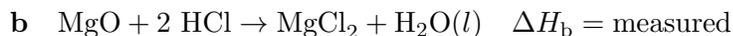
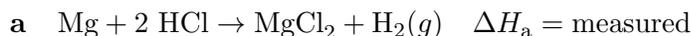
- 5 Record the mass of the clean, dry calorimeter to 0.01 g.
- 6 Put about 100 mL of water into it and record the mass to 0.01g.
- 7 Record the temperature of the water and calorimeter to 0.1°C.
- 8 Carefully record the temperature of the “boiling” water bath **with a 110°C thermometer** (to 0.5°C).
- 9 Carefully slide the hot metal from the test tube into the calorimeter. Do not hit the thermometer or add boiling water from the bath. Do not let the thermometer touch the metal.
- 10 Swirl the calorimeter gently and constantly.
- 11 Record the maximum temperature to 0.1°C.
- 12 Return the clean, dry, cool metal to the reagent bench.
- 13 Calculate the specific heat of your metal to three significant figures, using Eqns. 10a, 10b, and 10c, in units of J/g and J/mol.

$$\Delta H_1 + \Delta H_{\text{calorimeter}} + \Delta H_2 = m_1 c_{\text{water}}(T_{\text{final}} - T_1) + C_{\text{calorimeter}}(T_{\text{final}} - T_1) + m_2 c_2(T_{\text{final}} - T_2) = 0 \quad (10d)$$

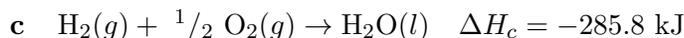
- 14 Using the molar mass and experimental specific heat of your metal, calculate the molar heat capacity, C , and compare it to the Dulong and Petit value of $3R$ ($R = 8.314 \text{ J/K} \cdot \text{mol}$).

Part 4: Heat of a Chemical Reaction

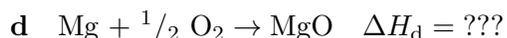
This experiment is discussed in Example 4. You will measure the heats of two reactions:



You also need a ΔH value for reaction c , which is from the literature.

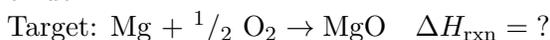


Using these ΔH values and Hess's Law, you can determine the ΔH for magnesium combustion (or formation), where magnesium metal is burned in oxygen.



- 1 Record the mass of the clean, dry calorimeter to 0.01 g.
- 2 Put 50 mL of distilled water into the calorimeter.
- 3 Add 25 mL of approximately 2 M HCl.
- 4 Record the mass of this water and acid combination to 0.01 g.
- 5 Take about 0.10–0.15 g of magnesium ribbon and record its mass to 0.01 g.
- 6 Take the initial temperature of the acidic water in the calorimeter to 0.1°C.
- 7 Add the metal, stir constantly, and record the maximum temperature reached to 0.1°C. The reaction takes a while, so be patient.
- 8 Repeat this procedure substituting about 0.30g of magnesium oxide for the magnesium ribbon.

The goal is to determine the heat of reaction for the combustion of magnesium to form the oxide.



- 9 Using Eqns. 13a, 13b, and 13c, calculate the experimental values of ΔH_a and ΔH_b reactions (a) and (b) to three significant figures.

$$\Delta H_1 + \Delta H_{\text{calorimeter}} + \Delta H_{\text{chemical reaction}} = m_1 c_{\text{water}}(T_{\text{final}} - T_1) + C_{\text{calorimeter}}(T_{\text{final}} - T_1) + \frac{m_2}{MM_2} \Delta H_{\text{reaction}} = 0 \quad (13d)$$

- 10 Using ΔH_a , ΔH_b , and ΔH_c , employ Hess' Law to **calculate the heat of reaction for the magnesium combustion reaction** (to three significant figures).

Note: Whenever you reverse a reaction, the sign of ΔH changes. That is because enthalpy is a state function; ΔH of state 2 to state 1 is equal in magnitude but opposite in sign of ΔH from state 1 to state 2.

- 11 Calculate the percent error in experimental value for the target reaction (literature value for the heat of formation of $\text{MgO}(s)$ -601 kJ) to three significant figures.
- 12 Calculate the percent error in your experimental ΔH_a and ΔH_b values (literature values are -462 kJ/mol for (a) and -146 kJ/mol for (b)) to three significant figures.

Waste Disposal: As per TA instruction; you will lose points if you do not dispose of waste properly.

REPORTING RESULTS

Complete your lab summary or write a report (as instructed).

Abstract

Results (final results are reported to three significant figures)

Calorimeter heat capacity

Heat of fusion of ice

Specific heats of metals

Heats of reaction from part 4 and for combustion of Mg.

Sample Calculations

Calorimeter heat capacity (part 1)

Heat of fusion of ice (part 2)

Specific heat of metals (part 3)

Heat of reaction for one of part 4 reactions (part 4)

Heat of magnesium combustion using Hess' Law (part 4)

Discussion

What you found out and how for each part

How good was your data (comparison to expected values, etc.)

Ideas to improve the accuracy in any or all of the procedures utilized in this experiment?

What conclusions can you draw?

Review