

# Calorimetry: Heat Capacities, Enthalpies (Heats) of Phase Transitions and Chemical Reactions, and Hess's Law

## Goal and Overview

The heat capacity of a simple constant-pressure calorimeter will be determined. The calorimeter will be used to find the heat of fusion of ice, the heat capacity of a metal, and the heats of several chemical reactions. The heat of reaction for the oxidation of Mg metal will be calculated using Hess's Law.

## 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

Reference material and textbook sections on thermochemistry, calorimetry, heat capacity, and enthalpy

## Introduction

It is not always convenient or straightforward to study the internal energy changes,  $\Delta E$ , of processes happening at constant pressure, such as those occurring in biological systems and in standard lab settings. Enthalpy,  $H$ , is a thermodynamic quantity that is defined as a system's internal energy,  $E$ , plus the product of pressure and volume,  $pV$ . At constant pressure, enthalpy is equivalent to the total heat content of the system,  $q_p$  (or  $q$  if it is known that constant pressure conditions are in effect).

$$H = E + pV \xrightarrow{\text{at constant } p} \Delta H = \Delta E + p\Delta V = q_p = q$$

Other important definitions include the system, the substance or substances undergoing the physical or chemical change, and the surroundings, the constituents of the thermodynamic “universe” that either provide heat to or absorb heat from the system.

Calorimetry is a technique that can be used to measure heat flow,  $q$ . A calorimeter is a calibrated measuring device that allows the amount of heat transferred to or from an object and/or during a physical or chemical change to be quantified.

In lab, it is often assumed that all of the heat transfers of interest remain within the calorimeter and its contents, such that the sum of the  $q$  terms equals zero. Heat transfer to or from the environment external to the calorimeter and its contents is assumed negligible.

Quantifying  $q$ : change in temperature ( $\Delta T \neq 0$ )

$q$  is proportional to the magnitude of the temperature change as well as heat capacity, the amount of heat required to change the system's temperature by 1°C. Specific heat capacity,  $c$ , is a per-gram value; molar heat capacity, per-mole.

$$q = \Delta H = C(T_f - T_{in}) = C_{general}\Delta T = mc\Delta T = nC\Delta T$$

Common heat capacity units

$C_{general}$	J/°C
$c$	J/g · °C
$C$	J/mol · °C

Quantifying  $q$ : constant temperature ( $\Delta T = 0$ )

The enthalpy change associated with the phase change or chemical reaction,  $\Delta h$  or  $\Delta H$ , is given in units of J/g (nonstandard) or kJ/mol (standard). Phase changes and chemical reactions that absorb heat energy are endothermic; those that release heat, exothermic.

$$q = m\Delta h = n\Delta H$$

There are four parts to this experiment.

First, you will calibrate your calorimeter to determine its heat capacity,  $C_{cal}$ , in J/°C, making sure that the value is within an acceptable range before proceeding. Second, you will determine the heat of fusion of ice,  $\Delta H_{fus}$ , in kJ/mol. Third, the heat capacity of a metal, either Al or Cu, will be determined, and the experimental  $C_{metal}$  will be compared to that predicted by the Law of Dulong and Petit. Fourth,  $\Delta H$  values for the reactions of Mg with

HCl and of MgO with HCl will be measured, with the results used in an application of Hess's Law to calculate  $\Delta H$  for the oxidation reaction of Mg by  $O_2$ .

## Equipment List

Styrofoam calorimeter, split stopper, thermometer  
Labeled beakers, large labeled test tube, hot plate  
Ice, copper or aluminum metal, magnesium ribbon, magnesium oxide  
~2 M HCl, deionized water  
Balance (pan and analytical)

## Procedure

You and your partner may be assigned to work with another pair of students. If this is the case, it is important that you share and record all of the values for the four parts of the procedure, including both sets of calibration data for the two calorimeters used, before leaving lab.

The experimental procedure must be divided as follows:

Pair 1	Pair 2
Part 1. $C_{cal\#1}$	Part 1. $C_{cal\#2}$
Using Calorimeter #1, $C_{cal\#1}$	Using Calorimeter #2, $C_{cal\#2}$
Part 2. $\Delta H_{fus}$ of ice	Part 3. $c_{Al\ or\ Cu}, C_{metal}$
Part 4a. $\Delta H_{4a, Mg+2HCl}$	Part 4b. $\Delta H_{4b, MgO+2HCl}$

The calorimeters have different heat capacities. You must use the correct  $C_{cal}$  value when calculating your results.

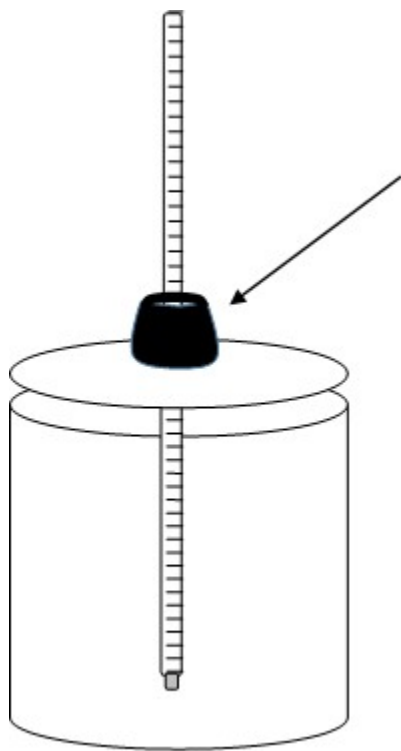
The pan balance, which reads to two decimal places, should be used for all masses except that of Mg (part 4a) and of MgO (part 4b).

For Mg and MgO, use the analytical balance (four decimal places).

Temperatures should be recorded to one decimal place.

Assume the specific heat capacity of liquid water,  $c_w$ , is 4.184 J/g · °C.

You will check your calorimeter out from your TA. You must return it to your TA clean and dry with no dents, divots, or punctures.



A split stopper is used to hold the thermometer in place so that the bulb is in the liquid inside the calorimeter but above the calorimeter's base.

### Caution

Gently **pull the split stopper open** to "pop" the thermometer into place or to adjust the position of the stopper along the thermometer's length.

**Do not push the thermometer without pulling the stopper open.** The thermometer will not slide through the hole in the stopper.

## Part 1. Heat capacity of the calorimeter

1. Record the mass of the calorimeter and lid to two decimal places.
2. Add ~100 mL of room temperature deionized water.
3. Record the mass of the calorimeter, lid, and water to two decimal places. Record room temperature to 1 decimal place.
4. Submerge a 150-mL beaker in the warm water bath ( $\sim 35.0^\circ$ ) for several minutes. Record the temperature of the water bath to one decimal place.
5. Take the calorimeter containing the room temperature water, lid, and thermometer (with split stopper in place) to the warm water bath.
6. **Quickly** scoop up ~100 mL of the warm water in the beaker equilibrated to the bath temperature and pour the water into the calorimeter. **Immediately** cover with the lid, insert the thermometer, and gently swirl. You **must** transfer the warm water to the

calorimeter very quickly so that the warm water does not have time to cool down appreciably.

- Record the final temperature reached by the mixture to one decimal place.
- Remove the thermometer and record the final mass of the calorimeter, lid, and both volumes of water to two decimal places.

You cannot complete the rest of the experiment before obtaining satisfactory results for part 1.

- Calculate the masses of the room temperature water and of the warm water by difference.
- Calculate  $C_{cal}$  to three significant figures.

$$q_{cal\#1\ or\ \#2} + q_{room\ temperature\ water} + q_{warm\ water} = 0$$
$$C_{cal\#1\ or\ \#2}(T_f - T_{RT}) + m_{RTW}c_w(T_f - T_{RT}) + m_{ww}c_w(T_f - T_{ww}) = 0$$

Note that this value is either  $C_{cal\#1}$  or  $C_{cal\#2}$ , depending on which parts of the experiment you are assigned (parts 2 and 4a or parts 3 and 4b).

**Do not go on to parts 2 – 4** before calculating the heat capacity of your calorimeter, which must be between 5.00 and 200. J/°C. Your TA must also check your calculation before you proceed. If the heat capacity is not within the allowed range, repeat part 1 until it is (see your TA for further instructions).

You must also get data and calculate  $C_{cal}$  for the calorimeter used by the pair of students with whom you are working.

## Part 2. $\Delta H_{fus}$ of ice

Calorimeter #1,  $C_{cal\#1}$

- Record the mass of the calorimeter and lid to two decimal places.
- Add ~100 mL of room temperature deionized water.
- Record the mass of the calorimeter, lid, and water to two decimal places. Record room temperature to 1 decimal place.

14. **Quickly** add ~25 g fully-frozen ice to the calorimeter and water. **Immediately** cover with the lid and insert the thermometer (with stopper in place).

15. Record the lowest temperature attained by the mixture to one decimal place.

16. Remove the thermometer and record the final mass of the calorimeter, lid, and water to two decimal places. Calculate the masses of room temperature water and of ice by difference.

17. Calculate the heat of fusion of ice in J/g to three significant figures. Assume ice melts at 0.0°C.

$$q_{cal\#1} + q_{room\ temperature\ water} + q_{ice\ melt} + q_{ice\ water} = 0$$
$$C_{cal\#1}(T_f - T_{RT}) + m_{RTw}c_w(T_f - T_{RT}) + m_{ice}\Delta h_{fus} + m_{ice}c_w(T_f - 0.0^\circ\text{C}) = 0$$

18. Convert to kJ/mol and calculate the percent error in your experimental result relative to a literature value of +6.01 kJ/mol.

$$\Delta h_{fus} \text{ in } \frac{\text{J}}{\text{g}} \times \frac{18.02 \text{ g (water)}}{1 \text{ mol ice (water)}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \Delta H_{fus} \text{ in } \frac{\text{kJ}}{\text{mol}}$$

$$\% \text{ error} = \left| \frac{\text{literature value} - \text{experimental value}}{\text{literature value}} \right| \times 100\%$$

### Part 3. Specific heat capacity of a metal and the Law of Dulong and Petit

Calorimeter #2,  $C_{cal\#2}$

Begin the temperature equilibration of the metal **before** calibrating the calorimeter (part1).

#### Caution

Steam, boiling water, hot glassware, hot metal, and hot plates surfaces can cause severe burns. Please be very careful.

Do not leave the hot plate and boiling water bath completely unattended. Keep other equipment at a safe distance.

Autoclave gloves are not heat-proof and are suitable for only short exposures to heat.

19. Obtain ~30 g Al or Cu metal and record which type of metal you have chosen.

20. Record the mass of metal to two decimal places.

21. Carefully slide the metal pieces into a large labeled test tube. Place the test tube in a water bath made in a 400-mL beaker. The level of the water in the bath should be higher than the level of the metal in the test tube.

22. Place the bath (containing the test tube holding the metal) on a hot plate and heat to gentle boiling for at least 20 – 30 minutes so that the metal can equilibrate to the temperature of the boiling water.

23. Record the temperature of the boiling water to one decimal place.

After you have completed part 1 successfully and calculated  $C_{cal\#2}$ :

24. Record the mass of the calorimeter and lid to two decimal places.

25. Add ~100 mL of room temperature deionized water.

26. Record the mass of the calorimeter, lid, and water to two decimal places. Record room temperature to 1 decimal place.

27. Take the calorimeter containing the room temperature water, lid, and thermometer (with split stopper in place) to your boiling water bath.

28. **Quickly and carefully, using the autoclave glove (or hot mitt)**, gently pour the hot metal into the calorimeter. **Immediately** cover with the lid, insert the thermometer, and gently swirl. You **must** transfer the hot metal to the calorimeter very quickly so that the metal does not have time to cool down appreciably.

29. Record the final temperature reached by the mixture to one decimal place.

30. Calculate the mass of room temperature water by difference.

31. Calculate the specific heat capacity of the metal in  $\text{J/g} \cdot ^\circ\text{C}$ .

$$q_{cal\#2} + q_{room\ temperature\ water} + q_{metal} = 0$$

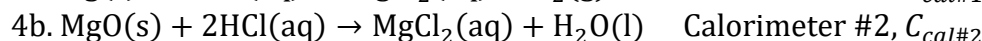
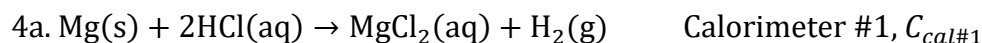
$$C_{cal\#2}(T_f - T_{RT}) + m_{RTW}c_w(T_f - T_{RT}) + m_{metal}c_{metal}(T_f - T_{boil}) = 0$$

32. Convert  $c_{metal}$  in  $\text{J/g} \cdot ^\circ\text{C}$  to  $C_{metal}$  in  $\text{J/mol} \cdot ^\circ\text{C}$  using the molar mass of the metal (26.98 g/mol Al or 63.55 g/mol Cu).

33. Calculate the percent error in your experimental result relative to  $C_{metal} \approx 3R = 3 \times 8.314 \text{ J/mol} \cdot \text{K} = 24.94 \text{ J/mol} \cdot \text{°C}$ . This value is based on the original law proposed in 1819 by French physicists Pierre Louis Dulong and Alexis Thérèse Petit (°C and K are equivalent in size).

Please make sure to return the metal clean and dry to the correct container on the reagent counter.

#### Part 4. $\Delta H_{reaction}$



You will experimentally determine  $\Delta H_{4a}$  and  $\Delta H_{4b}$ .

Given  $\Delta H_{4c} = -286 \text{ kJ/mol}$  for  $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$ , you will apply Hess's Law to find  $\Delta H_{4d}$  for  $\text{Mg(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{MgO(s)}$ .

Part 4a.  $\Delta H_{4a}$  for  $\text{Mg(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$  using Calorimeter #1,  $C_{cal\#1}$

34. Record the mass of the calorimeter and lid to two decimal places.

35. Add ~50 mL of room temperature deionized water first.

36. Take ~25 mL of ~2 M HCl in a labeled beaker. Add the acid to the water in the calorimeter.

37. Record the mass of the calorimeter, lid, and water-acid mixture to two decimal places. Record room temperature to 1 decimal place.

38. Take ~0.1200 g Mg ribbon (please close the jar) and record its mass on the analytical balance to four decimal places.

39. Add the Mg ribbon to the water-acid mixture in the calorimeter. **Immediately** cover with the lid, insert the thermometer, and gently swirl. Record the maximum temperature reached to one decimal place (be patient).

40. Calculate the mass of the water-acid mixture by difference and find the total mass of the solution in the calorimeter.

$$m_{solution} = (\text{mass water} + \text{acid}) + \text{mass Mg}$$



41. Calculate  $\Delta h_{4a}$  in J/g Mg to three significant figures. Assume that the heat capacity of the solution is equal to that of water. Convert to  $\Delta H_{4a}$  in kJ/mol and find the percent error to three significant figures.

$$q_{cal\#1} + q_{solution} + q_{reaction\ 4a} = 0$$

$$C_{cal\#1}(T_f - T_{RT}) + m_{solution}c_w(T_f - T_{RT}) + m_{Mg}\Delta h_{4a} = 0$$

$$\Delta h_{4a} \text{ in } \frac{\text{J}}{\text{g Mg}} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \Delta H_{4a} \text{ in } \frac{\text{kJ}}{\text{mol}}; \Delta H_{4a,lit} = -462 \frac{\text{kJ}}{\text{mol}}$$

Please do not pour the solution down the drain. Use the liquid waste container.

Part 4b.  $\Delta H_{4b}$  for  $\text{MgO}(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l)$  using Calorimeter #2,  $C_{cal\#2}$

42. Record the mass of the calorimeter and lid to two decimal places.

43. Add ~50 mL of room temperature deionized water first.

44. Take ~25 mL of ~2 M HCl in a labeled beaker. Add the acid to the water in the calorimeter.

45. Record the mass of the calorimeter, lid, and water-acid mixture to two decimal places. Record room temperature to 1 decimal place.

46. Mass out ~0.3000 g MgO solid in a weigh boat on the analytical balance. Record the mass to four decimal places. Please make sure to keep the balance and balance area clean.

47. Add the MgO solid to the water-acid mixture in the calorimeter. **Immediately** cover with the lid, insert the thermometer, and gently swirl. Record the maximum temperature reached to one decimal place (be patient).

48. Calculate the mass of the water-acid mixture by difference and find the total mass of the solution in the calorimeter.

$$m_{solution} = (\text{mass water} + \text{acid}) + \text{mass MgO}$$

49. Calculate  $\Delta h_{4b}$  in J/g MgO to three significant figures. Assume that the heat capacity of the solution is equal to that of water. Convert to  $\Delta H_{4b}$  in kJ/mol and find the percent error to three significant figures.

$$q_{cal\#2} + q_{solution} + q_{reaction\ 4a} = 0$$

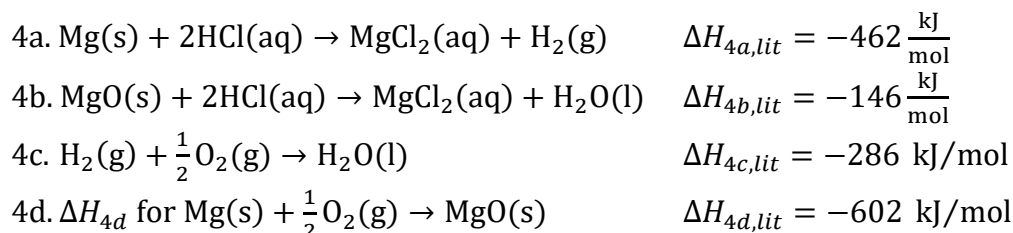
$$C_{cal\#2}(T_f - T_{RT}) + m_{solution}c_w(T_f - T_{RT}) + m_{MgO}\Delta h_{4b} = 0$$

$$\Delta h_{4b} \text{ in } \frac{\text{J}}{\text{g MgO}} \times \frac{40.31 \text{ g MgO}}{1 \text{ mol MgO}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \Delta H_{4b} \text{ in } \frac{\text{kJ}}{\text{mol}}; \Delta H_{4b,lit} = -146 \frac{\text{kJ}}{\text{mol}}$$

Please do not pour the solution down the drain. Use the liquid waste container.

50. In 1840, Hess stated that the heat absorbed or released by a chemical reaction is the same regardless of whether the reaction takes place in one step or in more than one, so the sum of the  $\Delta H$  values for the steps equals the  $\Delta H$  for the overall reaction.

Hess's Law makes it possible to determine enthalpies of reactions that would be difficult to measure experimentally. Apply Hess's Law to calculate  $\Delta H_{4d}$  to three significant figures using your experimental values for  $\Delta H_{4a}$  and  $\Delta H_{4b}$ , along with given value for  $\Delta H_{4c}$ .



Follow your TA's instructions regarding waste disposal. Please make sure to give your calorimeter to your TA.

All equipment and glassware should be washed thoroughly using 1) soap and tap water, 2) tap water rinses, and 3) a final rinse with deionized water.

## Results / Sample Calculations

$C_{cal\#1}$  and  $C_{cal\#2}$

$\Delta H_{fus}$  of ice, % error

$c_{metal}$ ,  $C_{metal}$ , % error relative to 3R

$\Delta H_{4a}$ ,  $\Delta H_{4b}$ , and  $\Delta H_{4d}$ , % error

Complete the online inlab or write a lab report as directed by your TA.

## Discussion Questions and Review Topics

What did you find and how did you do it?

What were the primary sources of error? How valid were the assumptions made, including that all of the heat transfer remained within the calorimeter and its contents? How could the accuracy of the results be improved? What conclusions can you draw about the experimental method and your results?