

Thermochemistry: Calorimetry and Hess's Law

Some chemical reactions are endothermic and proceed with absorption of heat while others are exothermic and proceed with an evolution of heat. The magnitude of the heat change is determined by the particular reaction of interest, as well as by the amount of reactants consumed.

The change in enthalpy, ΔH , is the heat (q_p) associated with a reaction at constant pressure, in which no work is involved other than "expansion work" or "compression work", associated with volume changes of the system (PV work):

$$q_p = \Delta H$$

The value of ΔH is a characteristic and important property of the reaction; convenient sets of units for the enthalpy is kJ/(mole of a component of the reaction). These units emphasize that enthalpy is an extensive property. Enthalpies of reaction (often called "heats of reaction") are usually tabulated for reactions occurring isothermally (at constant temperature), usually 25 °C. As long as the temperature change is not very large, the assumption that ΔH is constant with T is reasonable and within experimental error.

In this experiment, you will use an **adiabatic**, solution calorimeter, to determine enthalpies of reaction.

The Adiabatic Calorimeter

An **adiabatic** calorimeter is a device so well thermally insulated that the transfer heat across the boundary between the calorimeter and its surroundings is effectively zero during the experiment. In practice, perfect insulation is never achieved, but the error can be minimized through proper data treatment.

In part I of this experiment, the adiabatic calorimeter consists of a double Styrofoam cup fitted with a thermometer calibrated in tenths of a degree (permitting temperatures to be estimated to about $\pm 0.02^\circ\text{C}$) and a single, inverted Styrofoam cup (with a small hole for the thermometer) as a lid. It is crude, but very effective because of the excellent insulating properties of Styrofoam.

The heat exchanged between the reaction (ΔH) and the surroundings (adiabatic calorimeter) can be determined from:

$$\Delta H = -C_{\text{calorimeter}}\Delta T_{\text{calorimeter}}$$

where heat capacity, $C_{\text{calorimeter}}$, is the heat (of reaction) required to raise the temperature of the calorimeter by one degree. It will have contributions from the thermometer, the cups, the lid, and, **most importantly**, the water (solvent) in the calorimeter. In fact, we will assume that the contribution of the water in the calorimeter greatly outweighs **all** other contributions. The equation can then be written as:

$$\Delta H = -C_{\text{water}}\Delta T_{\text{calorimeter}}$$

Since the specific heat capacity, s , of water ($4.184 \text{ J/g}\cdot^\circ\text{C}$) is a well known quantity, all that is required to obtain the heat capacity of an aqueous solution calorimeter is to determine the (approximate) mass of water in it and use

$$\Delta H = -m_{\text{water}}s_{\text{water}}\Delta T_{\text{calorimeter}}$$

Key techniques for obtaining accurate results are starting with a dry calorimeter, measuring solution volumes precisely, and determining ΔT accurately. Careful experimenters deal with the first two items easily. The last is somewhat more difficult. The change in temperature is determined by measuring the initial temperature, T_1 , of the reactants, and the maximum (or minimum) temperature, T_2 , of the contents of the calorimeter during the exothermic (endothermic) reaction. The determination of a precise value for T_2 is complicated by the fact that a small heat exchange occurs between the surroundings and the contents of the calorimeter, both during the reaction and after its completion. The exact rate of exchange depends on the insulating properties of the calorimeter. A correction for this heat loss is made by an extrapolation of a temperature vs. time curve before and after the reaction (Figure 1).

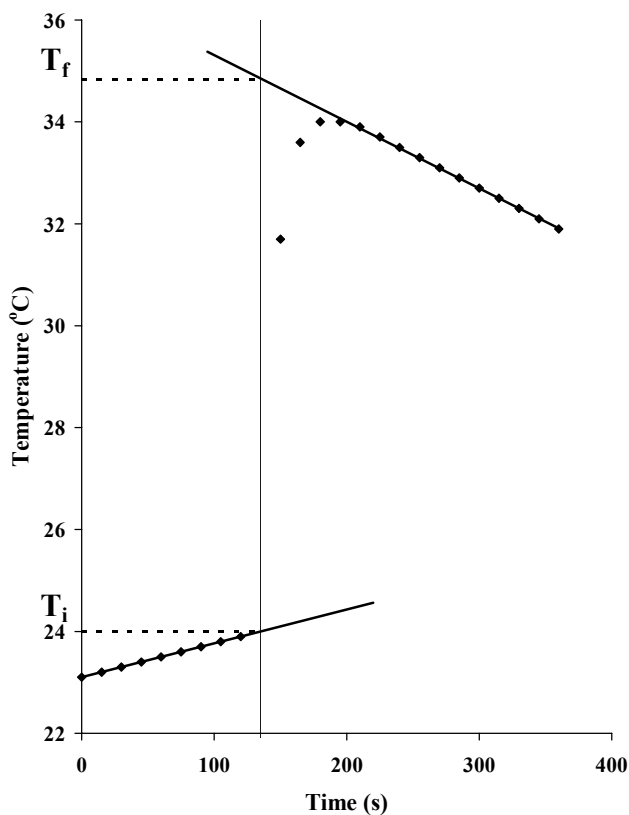
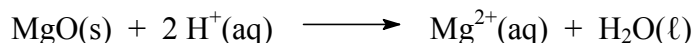
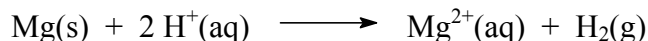


Figure 1: Temperature versus Time Curve. From extrapolation: $T_i = 24.0^\circ\text{C}$ and $T_f = 34.8^\circ\text{C}$.

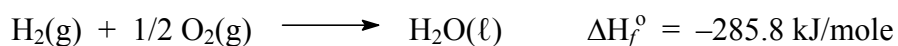
T_1 and T_2 are determined by extrapolating the linear portion of each curve forward or back to zero time (the time of mixing of the reactants in the calorimeter). The value of T_2 obtained in this manner is the temperature of the product solution, had the reaction occurred instantaneously with no enthalpy loss to the surroundings. The T_1 curve is greatly exaggerated, and will probably be horizontal.

In part I of this experiment, we will use an adiabatic, solution calorimeter to determine ΔH of the following reactions (with HCl as the proton source)

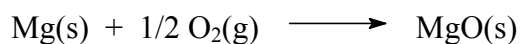


Hess's Law and Heat of Formation of MgO(s)

Hess' Law is a statement of the fact that ΔH is a state function; independent of path. If a reaction can be carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps. If we include the heat of formation of liquid water

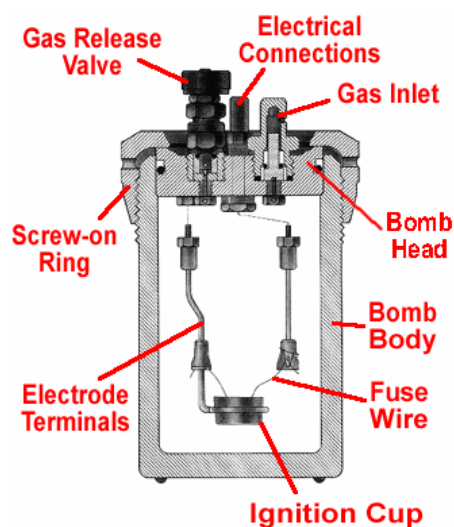
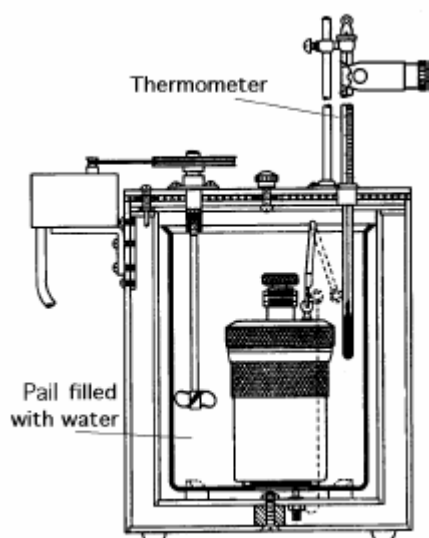


Hess's Law can be used, along with the two reactions studied in this experiment, to find the heat of formation (ΔH_f°) of MgO(s)



Bomb Calorimeter

In 1881, Pierre Berthelot devised a closed container he called a bomb, based on the fact that many substances, including hydrocarbons, will react easily with oxygen. The bomb calorimeter used today works by burning a hydrocarbon (or in our case, Mg) in high pressure oxygen in a stainless steel container. The stainless steel container is surrounded by water and the heat evolved by the reaction is absorbed by the surrounding water. By measuring the temperature change of the water, ΔH can be determined.



In part II, we will use a bomb calorimeter to find ΔH_f of MgO(s) directly. We will compare the two values from part I and II.

Part I

Procedure

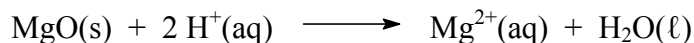
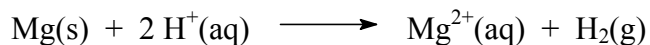
1. Rinse and dry a coffee-cup calorimeter and a thermometer. Place a stir bar in the cup and center the calorimeter on a stir plate.
2. Cut an 18 cm length of Mg ribbon and clean it with steel wool (to remove the oxide layer) until it is shiny and silver colored. Coil the ribbon loosely around a pencil. Weigh the ribbon in a tared 50.0-mL beaker (± 0.1 mg).
3. Pipet 100.0 mL of 1.0 M HCl solution into the calorimeter.
4. Start the stirrer so that it mixes thoroughly, but does not splash. Make sure the thermometer bulb is completely submerged in the HCl solution. Record the temperature initially (± 0.1 °C) and every 30 seconds for 4 minutes.
5. After 30 seconds from the last reading, lift the lid, add the Mg ribbon, and quickly replace the lid. 30 seconds after the Mg was added, record the temperature and continue to record the temperature every 30 seconds for 10 minutes.
6. Clean and dry the calorimeter for the MgO reaction.
7. Measure 1.6 g MgO (± 0.1 mg) in a weighing vial with a cap. Handle the vial and cap with Kimwipes to avoid changing the mass with fingerprints. Close the lid tightly to prevent the MgO from absorbing water from the air.
8. Repeat steps 3 and 4.
9. After 30 seconds from the last reading, lift the lid, pour the MgO into the HCl solution (Kimwipe), and quickly replace the lid. Replace the cap on the MgO vial.
10. 30 seconds after the Mg was added, record the temperature and continue recording the temperature, every 30 seconds, for 10 minutes.
11. Weigh the MgO vial and cap to determine how much MgO was added (by difference).

Part II

We will do this part as a group, with the procedure explained as we go. Read the handout “The Bomb Calorimeter” for an overview of the process.

Questions

1. Find the ΔH_f° values (textbooks, CRC Handbook of Chemistry and Physics, etc.) to calculate a literature value of the enthalpy change for the reactions



2. What is the purpose of measuring the temperature of the calorimeter for several minutes before and after the reaction?
3. In an adiabatic calorimetry experiment, 100 mL of 0.500 M HCl was added to 100 mL 0.500 M NaOH to produce 200 mL solution. A temperature increase of 3.38 °C was measured. Calculate the heat of reaction **per mole of NaCl produced**.

Data Treatment

1. Using a graphing program, such as EXCEL, find ΔT for the reactions performed in the coffee-cup calorimeter by plotting temperature versus time and extrapolating from the graph (as in Figure 1).
2. Calculate ΔH for the reaction of Mg with H^+ and the reaction of MgO with H^+ assuming 100.0 mL of 1.0 M HCl solution is approximately 100.0 g of water. Assume $C_{\text{cal}} = C_{\text{water}}$. Be sure to include the proper **sign** of the ΔH .
3. Use Hess's Law, with the two values above and the heat of formation reaction of $\text{H}_2\text{O}(\ell)$ to find ΔH_f° of MgO.
4. Use the bomb calorimeter data to find ΔH_f° of MgO.
5. Find a literature value of ΔH_f° of MgO and calculate the percent error of both the Hess's Law value and the bomb value.