THERMOCHEMISTRY HEAT OF REACTION, HESS'S LAW, AND HEAT OF FUSION

OBJECTIVES: a) To measure enthalpies of three different reactions using constant pressure calorimetry.

- b) To verify the application of Hess's Law.
- c) To measure the heat of fusion of ice.

INTRODUCTION

Many thermodynamic energy values of chemical and physical processes are obtained through (or derived from) calorimetric measurements (<u>Calorimetry</u>: "Measure of heat and energy"). There are two types of calorimeters:

- 1. <u>Constant volume calorimeters</u>: Among other purposes, this type of calorimeter is used to measure the energy value of different foods (the "Calories" with capital "C"- that appear in Nutrition Facts tables on cereal boxes and other foods).
- 2. <u>Constant pressure calorimeters</u>: This type of calorimeter allows to measuring enthalpy values of chemical and physical processes - after several interesting calculations steps (enthalpies are ΔH of processes and are related to "exothermic" and "endothermic" terms).

It is very easy to design a **constant pressure calorimeter**; one just needs to have one or two polystyrene (Styrofoam®) coffee cups and a thermometer; that's all!

The main concept to understand when performing calorimetric measures is that heat (i.e. energy) is simply exchanged from a substance to another; but if these substances are confined into an isolated system, all the energy changes become directly measurable.

Our model is very simple: our isolated container becomes our "**system**" and the latter (in theory) does not allow any heat exchange with the "**surrounding**". All the energy exchanges happen within the system.

In this experiment, we will first measure the heat of three different reactions involving calcium metal, water, a strong acid and a strong base. A fourth process (a physical process) will also be studied; this one will involve measurement of the heat of fusion of ice. At the end of the experiment, it will be possible to compare all these heats (enthalpies) of reaction and fusion with literature values in order to evaluate the reliability of the method. The results are generally very convincing.

Parts A, B, and C: Heats of reaction

In these parts of the experiment, you will measure the enthalpy change, ΔH , of each of the three following reactions:

(1)
$$H_3O^+(aq) + OH^-(aq) \rightarrow 2 H_2O(l)$$
 ΔH_1
(2) $Ca(s) + 2 H_2O(l) \rightarrow Ca^{2+}(aq) + 2 OH^-(aq) + H_2(g)$ ΔH_2
(3) $Ca(s) + 2 H_3O^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g) + 2 H_2O(l)$ ΔH_3

When a reaction takes place at constant pressure, the heat released or absorbed is called the enthalpy change and is symbolized by ΔH . This quantity is negative for an exothermic reaction and positive for an endothermic reaction. You will use a constant-pressure calorimeter, simply a container with insulating walls (so that no heat transfer occurs across them to the surroundings) and which contains a thermometer. For the sake of this experiment, we will consider that the heats absorbed by the calorimeter and by the thermometer are negligible (relatively too small to be taken into account, but this can be an excellent source of discussion in a laboratory report). The specific heat (c) of each solution in this experiment is assumed to be the same as that of pure water, i.e. 4.184 J/g °C. The equation governing the experiment is therefore:

$$q = m \cdot c \cdot \Delta T$$

where: q = the heat released
c = specific heat of the solution
m = mass of water (or solution)
 $\Delta T = T_{\text{final}} - T_{\text{initial}}$

Note that equations of reactions (1) and (2) can (after a bit of manipulation) be summed up to give the equation of reaction (3), according to Hess's Law. You will therefore measure ΔH for each of these three reactions and then calculate ΔH_3 (calc) from the values you obtained for ΔH_1 and ΔH_2 . In order to verify Hess's Law, you will compare this calculated value of ΔH_3 with the one you directly measured for this reaction during the experiment, ΔH_3 (expt).

Part D: Heat of fusion of ice

In this part of the experiment, we will measure the heat (enthalpy) of fusion of ice. To do so, we will simply melt a certain amount of ice in an amount of hot water; only two substances will be involved: $H_2O(s)$ and $H_2O(l)$. There will be energy exchange between the two WITHIN our isolated container (our "system"). For the sake of the calculations, we can assume that the ice is initially at 0°C, and the hot water will need to be at an initial temperature higher that 25°C (this initial hot water temperature will be measured before adding the ice). When ice is put in hot water, it will melt and the "cold" liquid water produced will instantaneously mix with the hot water. This will naturally cool down the hot water. In other words, the hot water provides the heat to melt the ice and warm up the "cold" water produced by the ice. There will be a lot of heat exchanges and everything will be easily measurable.

To solve any kind of calorimetric calculations, one must ask himself/herself the question "Where does the heat go?" "How is it exchanged?" "What substance will exchange heat with what other ones?" "Which substance will require heat and which one will release heat?"

Firstly, ice will need heat to melt; this is the heat of fusion, q_{fus} (what we want to determine). Then, the "cold" water (produced by molten ice) will warm up due to the hot water: $q_{cold water}$, abbreviated q_{cw} . All this is because the hot water will provide the required energy by cooling down. So hot water will also exchange energy; this is symbolized by $q_{hot water}$, abbreviated q_{hw} .

Hot water and ice being into our isolated container, and assuming that the latter does not release any heat in the surrounding, then the sum of all the heats exchanged during the process will sum up to 0. Here is the "algebra" (math) that relates all this together:

$$q_{fus} + q_{cw} + q_{hw} = 0$$
Equation 1

Since we want to find q_{fus} , we can isolate this parameter from the equation above, we get:

$$q_{fus} = -(q_{cw} + q_{hw})$$
 Equation 2

The q_{cw} and q_{hw} processes correspond to temperature changes in substances (water warming up and water cooling down). For each one of these water temperature changes, we can use the mathematical formula below to calculate the energy exchanged during the respective warming and cooling of water (this equation was introduced in parts A, B et C) :

$$q = m \cdot c \cdot \Delta T$$
Equation 3

Where **c** is the specific heat of water (in J $^{\circ}C^{-1}$ g⁻¹); $C_p = 4,184$ J $^{\circ}C^{-1}$ g⁻¹ for H₂O (*I*), *m* is the mass of water (in grams), and

 ΔT is the temperature change of water = T_{final} - T_{initial} (in °C or in K). **N.B.** It does not matter here if the temperature change is expressed in °C or in K since it is a **change** ΔT .

To calculate the masses, we can assume that the density of water is 1.00 g mL⁻¹ for hot and cold water (this shall induce a small systematic error but that can be discussed by students in their report). Initial and final temperatures will directly be measured (but we will assume that the initial temperature of cold water is 0°C since the latter comes from the ice that will melt).

With all these measurements and proper calculations (a good challenge for students), we can obtain q_{fus} for the mass of ice that was used. To get the heat of fusion of ice by gram, the value of q_{fus} just need to be divided by the mass of ice. According to energy data in textbooks, the heat of fusion of ice is of 333 J g⁻¹. Shall we be close or far from this value? This is what we will see in this experiment.

If you prefer to get the heat of fusion value in kJ/mol, just multiply by the molar mass of water (18.016 g/mol) and divide by 1,000 J/kJ to convert. The value of ΔH_{fus} of ice shall then be close to 6,0 kJ/mol.

Each year, on average, all the data of my students converged well to the expected ΔH_{fus} value; this is an overall great experience involving stoichiometric and thermochemical calculations for the students.

CHEMICALS

- Hydrochloric acid solution (HCI) (1.00 mol/L)
- Sodium hydroxide solution (NaOH) (1.10 mol/L)
- Phenolphthalein indicator
- Calcium metal (Ca)
- Water and crushed ice

EQUIPMENT NEEDED

- 50-mL, 100-mL and 250-mL Beakers
- 50-mL and 100-mL Graduated cylinders
- Weighing bottle
- Constant-pressure calorimeter (two Styrofoam coffee cups)
- Thermometer and Thermometer clamp
- Timer

PROCEDURE

The teaching assistant or laboratory supervisor will demonstrate the use of the calorimeter.

Part A: Reaction of Strong Acid with Strong Base

Weigh a clean and dry loose Styrofoam cup to the nearest 0.01 g. Using a 50-mL graduated cylinder, transfer 45.0 mL of the 1.00 mol/L HCI solution into the cup. Place the cup containing the HCI solution into the other cup of the calorimeter that fits into a 250-mL beaker to keep the apparatus stable; see picture below (**N.B.** In the picture, a burette clamp is used to hold the thermometer but it is better, however, to use a proper thermometer clamp to do so). Let the temperature stabilize then record it. Remove the thermometer from the cup, rinse it with distilled water, and dry it with a piece of paper towel.



Rinse your 50-mL graduated cylinder a couple of times with distilled water, shake dry, and then measure 45.0 mL of the 1.10 mol/L NaOH solution in the 50-mL graduated cylinder. Insert the thermometer in the NaOH solution (in the cylinder) and verify its temperature. Ideally, the temperatures of both solutions must agree to within 0.5 °C. If they do not, either cool the basic solution under running water or heat it by gripping the cylinder with your hands. Re-check the temperatures if required.

When the temperatures of the two solutions agree to within 0.5°C, hold the thermometer in the calorimeter using the clamp, then quickly add the NaOH solution to the HCI solution. Start timing and make sure you constantly and gently STIR (or SWIRL) the solution in the calorimeter. The temperature of the latter will rise very rapidly. Read and record the temperature every 10 seconds for the first minute and then every minute for two additional minutes for a total time of three minutes.

After three minutes, carefully remove the first cup containing the solution from the calorimeter and weigh it to the nearest 0.01 g. Add two drops of phenolphthalein solution to make sure the solution is basic. Rinse and dry the thermometer as before. Rinse the first cup of the calorimeter and set it aside to drain.

Part B: Reaction of Calcium with Water

Weigh again the clean and dry loose Styrofoam cup of the calorimeter to the nearest 0.01 g. Rinse your 50-mL graduated cylinder a couple of times with distilled water and shake dry. Using the 50-mL graduated cylinder, add 2 times 40.0 mL (i.e. 80.0 mL) of distilled water into the Styrofoam cup. Place the cup containing distilled water into the other cup of the calorimeter.

Weigh a clean and dry weighing bottle to the nearest 0.001 g (or to the 0.0001 g, if possible). Add about 0.4 g of calcium to the weighing bottle and reweigh it with the same precision (get the mass of calcium to 3 or 4 significant figures).

Prepare the same setup as Part A (i.e. put the two cups together in a 250-mL beaker and hold the thermometer in the calorimeter using a clamp). Let the temperature stabilize then record the initial temperature of distilled water. Add the calcium to the calorimeter, start timing and make sure you STIR (or SWIRL) the solution constantly. After 30 seconds, record a first value of temperature, and then record it every 30 seconds for a total time of 4.5 minutes.

After 4.5 minutes, carefully remove the first cup containing the solution from the calorimeter and weigh it to the nearest 0.01 g. Rinse and dry the thermometer as before. Discard the solution, rinse the first cup of the calorimeter and set it aside to drain.

Part C: Reaction of Calcium with Strong Acid

Weigh again the clean and dry loose Styrofoam cup of the calorimeter to the nearest 0.01 g. Using the 50-mL graduated cylinder, add 2 times 40.0 mL (i.e. 80.0 mL) of the 1.00 mol/L HCI solution. Place the cup containing the HCI solution into the other cup of the calorimeter.

Weigh the clean and dry weighing bottle again to the nearest 0.001 (or 0.0001 g). Add about 0.3 g of calcium to the weighing bottle and reweigh it with the same precision.

Prepare the same setup as Part A (i.e. put the two cups together in a 250-mL beaker and hold the thermometer in the calorimeter using a clamp), let the temperature stabilize then record the initial temperature of the HCl solution before reaction. Add the calcium to the calorimeter and start timing (make sure you STIR (or SWIRL) the solution constantly). After 30 seconds, record a first value of temperature, and then record it every 30 seconds for a total time of 4.5 minutes.

After 4.5 minutes, carefully remove the first cup containing the solution from the calorimeter and weigh it to the nearest 0.01 g. Rinse and dry the thermometer as before. Discard the solution and rinse the first cup of the calorimeter and set it aside to drain.

Collect all your data on your Data/Observation sheets. From your temperature change measurements (that you can also plot as a heating curve on a "T <u>vs</u> Time" graph), find the **final temperature** for each reaction (*i.e.* the highest temperature you observed). Perform the necessary calculations.

Part D: Heat of fusion of ice

Prepare the same setup as Part A (i.e. put the two cups together in a 250-mL beaker and hold the thermometer in the calorimeter using a clamp). Your instructor should have pre-heated a big beaker of water to reach a temperature around 55 to 60°C). Carefully sample 100 mL of hot water using the 100-mL graduated cylinder and pour it into your calorimeter. Another beaker of crushed ice should also be available for you.

From now on, you must work as fast as possible but still carefully. Measure about 80-100 mL of crushed ice in a 100-mL beaker. One of the team member shall keep an eye on the thermometer. He/she shall first measure the **initial temperature** of the hot water. The other team member shall pour, all at once, the crushed ice into the calorimeter while carefully swirling the latter to uniformize the temperature change. The "temperature measurer" team member must be very attentive, as **the temperature will rapidly go down**. The lowest temperature (**final temperature**) will need to be noted (all data may also be plotted on a "T <u>vs</u> Time" graph to facilitate the process). All the ice will need to be molten; which may only take a few seconds if the water was very hot at the beginning.

We can assume that the density of hot water is 1.00 g mL⁻¹ (but this can be an important source of error to discuss in the report!). According to this assumption, and since you measured 100.0 mL of hot water, the value of m_{hw} can be estimated to 100.0 g. <u>QUESTION</u>: How can we correct or minimize this source of error?

Measure the mass of the Styrofoam cup with all the water in it then discard the water, dry the cup and measure its mass again (empty). The difference of mass will correspond to the total mass of water. By subtracting 100.0 g from this total mass (or the corrected mass of hot water), one can estimate the mass of ice that was used.

With all these numbers, one has all the data to fulfill the respective objectives of this experiment.

DATA/OBSERVATION SHEETS THERMOCHEMISTRY (CONSTANT PRESSURE CALORIMETRY)

	Part A		Part B	Part C	
Mass of cup	g	Mass of cup	g	g	
Mass cup + sol ⁿ	g	Mass cup + sol ⁿ	g	g	
Mass solution	g	Mass solution	g	g	
T _{initial} sol ⁿ HCI	°C	T _{initial}	°C	°C	
T _{initial} sol ⁿ NaOH	°C	Mass Ca (s)	g	g	
Average T _{initial}	°C				

Table 1: Masses and initial temperatures (Parts A, B and C)

Table 2	Temperature	changes	(Parts A	B and	4 C)
	remperature	changes	(I a I I 3 A)	, D and	,

	Part A		Part B		Part C
10 s	°C	30 s	°C	30 s	°C
20 s	°C	60 s	°C	60 s	°C
30 s	°C	1.5 min.	°C	1.5 min.	°C
40 s	°C	2.0 min.	°C	2.0 min.	°C
50 s	°C	2.5 min.	°C	2.5 min.	°C
60 s	°C	3.0 min.	°C	3.0 min.	°C
2 min.	°C	3.5 min.	°C	3.5 min.	°C
3 min.	°C	4.0 min.	°C	4.0 min.	°C
		4.5 min.	°C	4.5 min.	°C

Table 3: Masses and initial temperatures (Part I	D)
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Volume of hot water	mL
T _{initial} of hot water	°C
Density of hot water	g/mL
Calculated mass of hot water	g
T of cold water	Fatimated at 0.0°C
	Estimated at 0.0°C
Mass cup + water after experiment	Estimated at 0.0°C
Mass cup + water after experiment Mass empty cup	g g
Mass cup + water after experiment Mass empty cup Total masse of water	g g g

Table 4: Temperature changes (Part D)

	Trial 1		Trial 2
5 s	°C	5 s	°C
10 s	°C	10 s	°C
15 s	°C	15 s	°C
20 s	°C	20 s	°C
25 s	°C	25 s	°C
30 s	°C	30 s	°C
45 s	°C	45 s	°C
1 min.	°C	1 min.	°C
1.5 min.	°C	1.5 min.	°C