4. HESS'S LAW USING SOLUTION CALORIMETERS (PARR 1455 and PARR 6755 models).

GOALS

● Use calorimeters which are specially designed to measure enthalpies in processes involving solutions. Although its theory is very similar to regular calorimetry experiments that can be performed using Dewar flasks and regular thermometers, these calorimeters feature a very sensitive thermometric probe and, a simple and reliable apparatus to initiate the processes to be studied. They also have a small microprocessor for collecting data.

● Determine the calorimeter constant, also called equivalent in water, using an appropriate standard substance.

● Using Hess's Law, combine experimental data from reactions carried out in the calorimeter to determine the heat of formation of a compound (MgO) for which the formation reaction is difficult to perform.

● Use Hess's law again to determine the heat of hydration for an anhydride salt by measuring the solution enthalpies for the anhydride and hydrated salts.

THEORETICAL BACKGROUND

Heat of formation of magnesium oxide

The magnesium oxide enthalpy of formation is difficult to measure directly because it is difficult to carry out the corresponding reaction to 100% yield. In turn, applying the Hess law, it is possible to determine it, measuring the enthalpies of reaction of the following reactions:

$$(1) \qquad Mg(s) + 2H^{+}(aq) \Rightarrow Mg^{++}(aq) + H_2(g) \qquad \Delta H_1$$
$$(2) \qquad MgO(s) + 2H^{+}(aq) \Rightarrow Mg^{++}(aq) + H_2O(l) \qquad \Delta H_2$$

Hess's law gives us the enthalpy of the following reaction:

$$Mg(s) + H_2O(l) \Rightarrow MgO(s) + H_2(g)$$

from which the student should be capable of obtaining the MgO enthalpy of formation by searching for other necessary data in the bibliography.

Heat of hydration for the copper sulphate

Many salts, crystalline ionic substances, composed of metal cations and non-metal anions, form hydrates in the crystallisation process from their aqueous solution. The crystalline structure of the hydrates contains water molecules joined in specific places on the crystalline salt network, giving them very specific stoichiometry. For example, you are going to study the case of copper sulphate $CuSO_4$ that, in its hydrated form, maintains five molecules of water joined to the salt, so the hydrate formula can be expressed as $CuSO_4*5H_2O$.

Hydrates are generally stable at room temperature and energy is required to remove the water molecules they carry. The enthalpy difference between the hydrated salt and the anhydride salt is known as the enthalpy of hydration and it is the subject of this experiment. In the case of the $CuSO_4$, the process can be written as follows:

$$CuSO_4 + 5H_2O \Rightarrow CuSO_4 * 5H_2O$$

One of the methods to calculate the enthalpy for this process involves using Hess's law and combining the enthalpies that can be measured experimentally in a solution calorimeter, from the anhydride salt and the hydrated salt dissolving processes:

$$CuSO_4 * 5H_2O(s) + nH_2O(l) \Rightarrow CuSO_4(aq) + (5+n)H_2O(aq)$$
$$CuSO_4(s) + (5+n)H_2O(l) \Rightarrow CuSO_4(aq) + (5+n)H_2O(aq)$$

To carry out the process, the number *n* of mols of water should be large enough so that the presence of 5 more does not affect the heat of solvation.This is achieved by diluting the salts in dilutions of around one to one thousand parts, in terms of mols of salt to mols of water.

EXPERIMENTAL PROCEDURE

Material	**Reactants**
Parr Calorimeter	HCl
Mortar and pestle	MgO, Mg
100 mL graduated cylinder	TRIZMA
1 L Volumetric Flask	$CuSO_4$, $CuSO_4•5H_2O$

Handling the calorimeter and its calibration

Students should be familiar with the calorimeter model that they are going to use before starting this experiment, **referring to its instructions for use and calibrating the instrument according to the procedure described in these instructions**.

Heat of formation for the Magnesium Oxide

To determine the heat of formation for the MgO, the enthalpies from reactions (1) and (2) between the metal Mg and the MgO with HCl will be measured experimentally. In both cases, the acid will be in 0.5 M solution form, and one litre of this solution will be prepared using a one litre volumetric flask.

Both in the case of the metal Mg and the oxide, the quantities weighed will be of the order of one millimol using the plastic lid from the calorimeter measurement cell. 100 ml of 0.5 M hydrogen chloride will be put in the calorimeter's Dewar flask.

The procedure to measure the reaction heat is identical to what is followed in the case of calibration with the TRIZMA (see instructions for using the respective calorimeter).In the case of calorimeter PARR1455 you only use the data relating to the temperature change during the processes (Temp. Rise) to multiply it by the apparatus constant (*e*) and calculate the heat linked to the process:

$$Q_{process} = e\Delta T$$

Dividing by the reactant (Mg or MgO) mols, you obtain the integral heat. Make the necessary changes so that this magnitude is expressed in Jules/mol.

The experiments with the metal Mg and the MgO will be repeated three times. Between experiments, try to keep the plastic base of the measurement cell (where the reactants are weighed) and the actual glass cell <u>properly dry</u> (washing with acetone if necessary and drying with a hair-dryer).

Heat of hydration for the copper sulphate

When determining the enthalpy of hydration for the $CuSO_4$ experimentally, you measure the enthalpies of solution for the anhydride $CuSO_4$ and the pentahydrated $CuSO_4$. To do so, put 100 ml of deionised water in the calorimeter Dewar flask and on the part that closes the measurement cell, weigh out the right quantities of the anhydride and hydrated salt so that the dilution is as close as possible to 1:1000 (in mols).

In both cases, make sure that the salts are properly crushed so that they completely dissolve (check with the teacher in charge before using them). Use the mortar if needed.

The procedure to measure the reaction heat is identical to calibration with the TRIZMA (see instructions for using the respective calorimeter). In the case of calorimeter PARR1455 you only use data relating to temperature change during the process (Temp. Rise) to multiply it by the apparatus constant (e) and calculate the heat linked to the process:

$$Q_{process} = e\Delta T$$

Dividing by the reactant (anhydride or hydrated $CuSO_4$) mols, you obtain the integral heat. Make the necessary changes so that this magnitude is expressed in Jules/mol.

The experiments will be repeated three times for each salt. Between experiments, try to keep the plastic base of the measurement cell (where the reactants are weighed) and the actual glass cell <u>properly dry</u> (washing with acetone if necessary and drying with a hair-dryer).

Questions to be resolved

● Determine the heat of formation for the MgO and the heat of hydration for the $CuSO_4$. In each case, the result should be compared with information in the bibliography or on the internet, explaining any possible differences that might be found.