

EXPERIMENT 2: HEATS OF IONIC REACTIONS

Safety



Remember to do your risk assessment for this lab and the pre-lab questions.



You must wear safety glasses, a laboratory coat and fully enclosed shoes covering your forefoot, toe and heel at all times whilst in the laboratory during this

Introduction

Calorimetry, derives from the Latin word *calor* meaning heat, and the Greek *metry* meaning to measure (Harper 2000). Thus, it is the science of measuring amounts of heat. All calorimetric techniques are based on the measurement of heat generated or consumed by a sample, depending on whether exothermic or endothermic processes are involved.

A calorimeter can be a simple Styrofoam cup, because it is a container with insulated walls that prevents heat exchange with the environment. In order to measure heats of reactions, we enclose reactants in a calorimeter, allow the reaction to proceed, and measure the temperature change (ΔT). Then the heat released or adsorbed in the reaction can be calculated.

A calorimeter may be used under constant pressure (atmospheric), or constant volume, but its heat capacity must be measured. The heat capacity is the amount of heat required to raise the temperature of the entire calorimeter by 1 K, and it is usually determined experimentally just before or after the actual measurement of the heats of reaction. This is done by transferring a known amount of heat into the calorimeter and measuring its temperature increase. Because the temperature differences are often very small, sensitive thermometers are preferred for these measurements.

Theory

The investigation of thermodynamics leads to two fundamental definitions: the system and the surroundings. The system is that which is being measured, observed and investigated while the surroundings are everything else.

An isolated system is referred to as adiabatic, as there is no exchange of matter or energy between the system and its surroundings. The energy considerations of a reaction include heat (denoted q), which is the energy absorbed by the system, and the work done on the system (denoted w).

As heat is transferred into or out of a system this leads to a change in temperature, and the quantity of energy that causes a temperature change is determined with Equation 1.

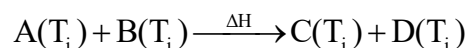
$$q = \sum c_p (T_f - T_i) \quad -(1)$$

Where q is the heat of the process, c_p is the heat capacity of the system at constant pressure, T_f is the final temperature and T_i is the initial temperature. The enthalpy of any process is the heat absorbed by the system at constant pressure.

Obtaining an Isothermal Enthalpy

The enthalpy of a reaction under isothermal conditions can be determined by conducting the experiment adiabatically, and then measuring the temperature change that occurs in the reaction vessel.

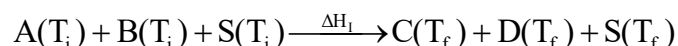
The isothermal reaction at temperature T_i can be expressed as follows:



Where ΔH is the enthalpy of the isothermal reaction for each mole of reaction as written.

In a calorimeter the system is insulated, and therefore no energy is lost to the surroundings. This is known as an adiabatic system and therefore in the calorimeter the energy of the reaction is used to heat the system with no loss.

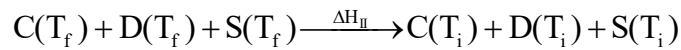
The adiabatic reaction can be expressed as follows:



Where ΔH_i is the enthalpy of the adiabatic reaction. A, B, C and D continue to be the reactants and products respectively and S is the parts of the system (thermometer, solvent, reaction vessel walls etc.) that maintain the same temperature as the reactants and products because of the insulated system.

Enthalpy however is a state function, and therefore independent of the steps taken to get to the final stage. Thus, the enthalpy of the isothermal reaction will be the sum of the enthalpy of any steps that start and finish in the same state.

Therefore in order to finish the adiabatic reaction under the same conditions as the isothermal reaction, the system merely needs to be cooled to the initial temperature.



ΔH_I and ΔH_{II} are the enthalpies of the alternate steps taken to go from the initial stage to the final stage of the isothermal reaction, and therefore as shown in Figure 1 the enthalpy of the isothermal reaction is the sum of these two values.

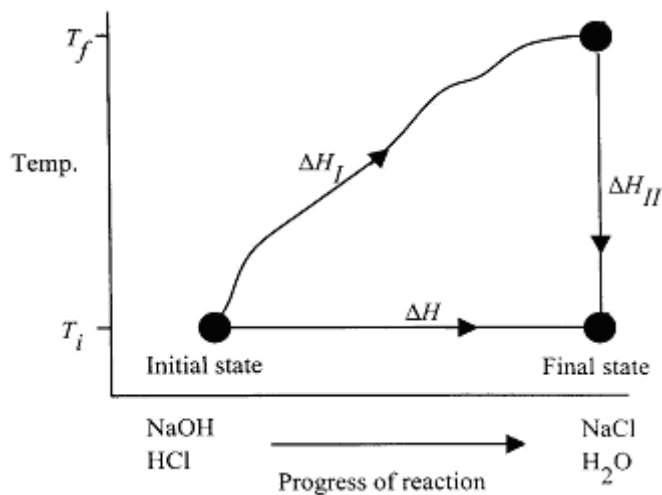


Figure 1 – Reaction Enthalpy Diagram. ΔH is the enthalpy of the isothermal reaction, ΔH_I is the enthalpy of the adiabatic reaction and ΔH_{II} is the enthalpy of the cooling step.

$$\Delta H = \Delta H_I + \Delta H_{II}$$

As stated previously an adiabatic reaction is a reaction contained in an isolated system, i.e. no energy is transferred out of the system. This means that the heat of the adiabatic step is 0, and therefore ΔH_I is also 0. The cooling step indicated in Figure 1 need not be performed, but rather the heat of Step II can be calculated by applying Equation 1.

$$\Delta H_{II} = \sum c_p (T_f - T_i)$$

where c_p is the heat capacity of the entire adiabatic system. This, therefore, means that if the temperature of the system at the beginning and end of the reaction is measured, the isothermal enthalpy can easily be calculated.

$$\Delta H = \Delta H_{II} = C_p(T_f - T_i)$$

Reaction Enthalpy Under Standard Conditions

Just as an isothermal enthalpy can be calculated from results that take a different series of steps, the enthalpy of a reaction under standard conditions can be determined from any isothermal energy of that reaction.

An alternative series of steps for the standard reaction to occur is: i) changing the system temperature from standard conditions to the experimental temperature, ii) proceeding with the reaction, iii) changing the temperature back to standard temperature.

As these three steps start with the reactants under standard conditions and finish with the products under standard conditions the sum of the enthalpies of these steps is equivalent to the enthalpy of the reaction proceeding under standard conditions. This is presented as Figure 2.

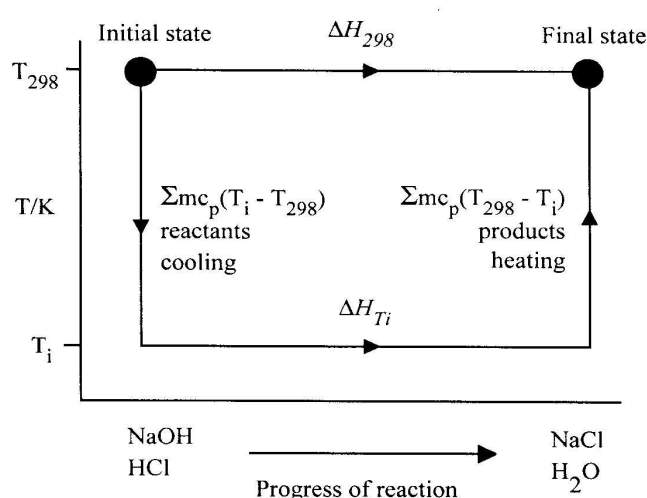


Figure 2 – Isothermal Reaction Enthalpy Diagram. Where ΔH_{T_i} is the isothermal enthalpy derived previously and ΔH_{298} is the standard enthalpy of the reaction.

Equation 1 can be applied once again in order to calculate the temperature change enthalpies as indicated in the diagram.

Experimental Factors

No experimental configuration is truly adiabatic, and in this case the stirrer adds energy to the system while the thermometer and non-ideal insulation allows heat to escape from the system. These factors produce fairly linear changes in temperature before and after the reaction occurs. In order to accurately account for these effects, the temperature must be measured for a period of time before the reactants are combined and for a period of time after the reaction has proceeded. Plotting this data and recording the relative time the reactants were combined allows the change in temperature to be more accurately determined as shown in Figure 3.

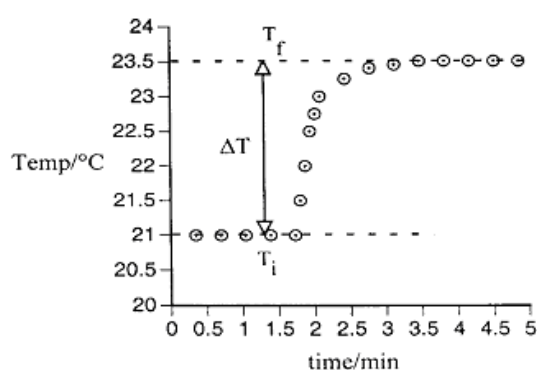


Figure 4a

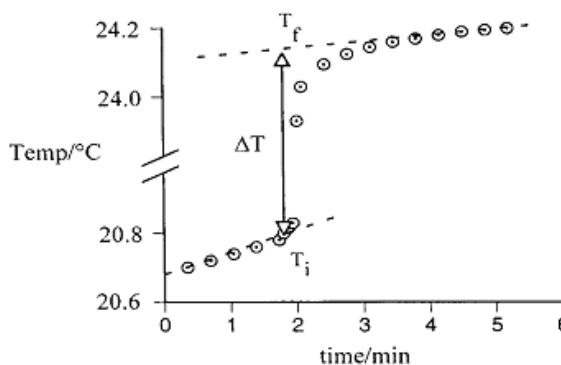


Figure 4b

Figure 3 – Temperature vs. Time and determination of ΔT .

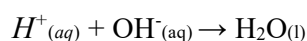
Learning Outcomes

On successful completion of this experiment, students will be able to:

- conduct simple isothermal experiments
- understand the importance of state functions
- use the concept of state functions to analyse their results

PRE-LAB Questions

1. What is a state function?
2. Construct a simple formula to convert between the molality and molarity of aqueous solutions.
3. From literature values of the standard enthalpy of formations, calculate the standard enthalpy of the reaction:



and obtain a literature value for the specific heat capacity of pure water. (i.e. you will need to do some research to get these values)

Experimental Procedure

The first part of the experiment is to determine the heat capacity of the calorimeter (i.e. calibrate your thermos):

1. Use a beaker to add 100 g of 1.500 molal NaOH solution into the calorimeter. Weigh the beaker, weigh in 100 g of solution and pour the solution into the calorimeter. Reweigh the beaker to determine the mass of residual solution.
2. Place a stirring bar in the calorimeter, and place it on a magnetic stirrer. Set for gentle agitation.
3. Set the calorimeter lid in place. Ensure the digital temperature probe is in the solution. The probe should not touch the calorimeter.
4. Calculate the precise mass of 1.500 molal HCl solution required to neutralise the mass of NaOH solution in the calorimeter.
5. Weigh this mass of HCl solution into a clean beaker as per step 1. Add a small excess (~1 gram) to ensure NaOH is the limiting reagent. Do not pour this into the calorimeter yet.
6. Record the temperature of the calorimeter contents every thirty seconds.
7. Check the temperature of the two solutions. Use warm and cold water to adjust the temperature of the HCl in the beaker to match that of the NaOH solution in the calorimeter by ± 0.5 °C.
8. When calorimeter temperature has been monitored over four minutes, add the HCl solution to the calorimeter. Accurately record the time of addition of reagent and continue with thirty-second temperature recordings for at least 5 minutes.
9. Reweigh the beaker to determine the exact mass of HCl solution added.
10. Repeat twice more, to obtain an accurate value for the calorimeter constant. Plot your results.

The enthalpy of this reaction is the same as that for the $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ reaction for which you should have a value from your pre-lab. Thus, we can use the temperature change, the known enthalpy value and the heat capacity of aqueous NaCl to determine our calorimeter constant. Firstly, determine how many moles of base you have (this will be the same number of moles of acid, neglect the small *additional* amount you added since the number of moles will be determined from the limiting reagent).

Next calculate the total heat in Joules that should be released from this reaction

The heat (q) released by the reaction is equal to the *negative* of the heat absorbed by the calorimeter and is equal to:

$$(C_{NaCl(aq)} + C_{calorimeter}) \times (T_{final} - T_{initial}) = -q$$

where C is the heat capacity and T is temperature (K). The heat capacity of the formed NaCl **in solution** can be calculated from the specific heat capacity. If the specific heat capacity of *aqueous* NaCl is $4.096 \text{ J g}^{-1} \text{ K}^{-1}$, how would you determine the heat capacity? What mass would you use?

- A. What is the average value of your calorimeter heat capacity and what is the error?
- B. Why don't you take the averages of the change in temperature?

Now perform the experiment using the reagent pairs shown in Table 1 in duplicate.

For upload:

1. Upload your answers to questions A and B
2. Upload your data
3. Calculate your heat capacity for the calorimeter

For report

Use the heat capacity for the calorimeter to determine the enthalpy of the reactions in Table 1 (in kJ mol^{-1}).

Table 1 – Reagent pairs

Enthalpy of ..	in calorimeter	in beaker
1. Neutralisation	1.500 molal NaOH	1.500 molal HNO ₃
2. Neutralisation	1.500 molal KOH	1.500 molal HCl
3. Neutralisation	1.500 molal KOH	1.500 molal HNO ₃
4. Dissolution	Water (100g)	NH ₄ NO ₃ solids (15 g)
5. Crystallization	Water (~300g)	Hand warmer pouch

Note: if you are doing experiment 5 with the hand warmer pouch, you will need to add enough water to cover 1/2 to 2/3 of the pouch, otherwise you may lose a lot of the heat from the top of the pouch rather than transfer the heat to the water. You should accurately measure how much water you have used for your experiment.

C. If the values for reactions 1-3 are different from each other and the literature value for $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$, why would that be?

Table 2 - Specific Heat Capacities

Substance	Molality (molal)	Specific Heat Capacity (J g ⁻¹ K ⁻¹)
KCl (aq)	1.5	4.074
NaCl (aq)	1.5	4.096
NaNO ₃ (aq)	1.5	4.081
KNO ₃ (aq)	1.5	4.059
NH ₄ NO ₃ (s)	-	4.180
Hand warmer pouch	-	Use the literature value you found for water

REFERENCES

Harper D 2000, *Online Etymology Dictionary – Calor*, viewed 27th January 2005,

Departure Checklist

A **two mark** deduction from the total mark for this experiment will apply if the checklist is not complete and your demonstrator has not initialed it.

My work area is clean and tidy		
I have cleaned and returned all glassware		
I have wiped down all common areas, such as fumehoods and sinks		
I have returned all the reagents used		
I have had my laboratory work signed off by my demonstrator		
I know the report deadline is:		
Demonstrator's initials		

	Absent	Developing	Competent	Proficient	Mastered
Has all PPE	0	0.25	0.5	0.75	1
Cleans all equipment prior to and post use	0	0.5	1	1.5	2
Works safely in lab and in a timely manner	0	0.5	1	1.5	2
Data collected is easy to see	0	0.5	1	1.5	2
Teamwork (equal sharing of workload)	0	0.25	0.5	0.75	1

Total:
