EXPERIMENT 9

Enthalpy Measurement in Chemical Reactions

INTRODUCTION:

Chemical and physical changes are often accompanied by heat evolution or absorption. A process in which heat is released to the surroundings is referred to as exothermic while one in which heat is absorbed from the surroundings is said to be endothermic. By measuring the quantity of heat evolved or absorbed in a given process, it is possible to infer important information about bond strengths and other parameters that are useful in developing an understanding of chemical reactivity. In this Unit, we will explore how these measurements can be made and how they can be applied.

In general, the condition for a process to occur (for it to be "spontaneous") is that

$$\Delta G < 0 \quad \text{(i.e. negative)}$$

where $$\Delta G = \Delta H \; - \; T(\Delta S)$$

The symbols have the following meanings:

ΔG: Gibb's Free Energy change
ΔH: Enthalpy Change
ΔS: Entropy Change
T: Absolute (Kelvin) Temperature.

Thus, it is ΔG, which includes an entropy component (ΔS), that determines whether a process is spontaneous, and not ΔH, which measures only heat energy changes.

In this experiment we will focus on four systems. First, the decomposition of hydrogen peroxide (H_2O_2) is studied, where the enthalpy of decomposition of 1 mole of hydrogen peroxide will be determined. This quantity is related to the strengths of the bonds in both H_2O_2 and its decomposition products. Second, the heat of hydration of anhydrous copper (II) sulfate is measured. This provides a measure of the strength of the bond between water molecules and a Cu^{2+} ion. Finally, an endothermic reaction, the dissolution of ammonium chloride in water, is investigated and the process is used to focus on the roles of heat energy and of entropy in influencing chemical and physical changes.

Thermochemical measurements are carried out using a calorimeter, which is basically a container that is well insulated so that heat exchange with the environment is prevented. For accurate work, rather sophisticated calorimeters are available; however, a simple but effective calorimeter can be improvised from a small Styrofoam coffee cup. This proves to be quite satisfactory for exploratory investigations such as those carried out here. Heat absorbed by or lost from the cup (calorimeter) is small and can be ignored here.

Chemicals & Equipment

Soup thermos & lid	stirring rod	temperature probe
Venier Labquest	Casserole dish	hot plate
Weighing boat	Graduated cylinder	10% H_2O_2
2.5 M KI	$CuSO_4.5H_2O$ (s)	NH_4Cl (s)

PROCEDURE:
Part I: Hydrogen Peroxide Decomposition

➢ Set up a clean empty calorimeter.

➢ Hydrogen peroxide is an extremely reactive substance. Even the dilute solution (10%) used in this experiment should be treated with caution. Contact with the skin or clothing should be avoided. Wash off any spills immediately with plenty of cold water.

➢ Using a graduated cylinder, add 25.0 mL of 10% H_2O_2 solution (available from the center bench or hood) and record the initial temperature of this solution in the calorimeter.

➢ Now add 2.0 mL of the 2.5 M KI solution provided. Potassium iodide serves as a catalyst for the decomposition of hydrogen peroxide according to the equation:

$$H_2O_2 \, (aq) \rightarrow H_2O \, (l) + 1/2 \, O_2 \, (g) + heat$$
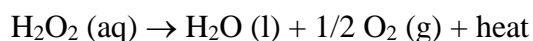
➢ Swirl gently to mix the solution in the calorimeter, and note the increase in temperature with time. Record the maximum temperature of the reaction mixture.

➢ After the decomposition reaction is complete, pour the contents of the calorimeter into a beaker and allow to cool. Measure the volume of this solution using a graduated cylinder.

CALCULATIONS:
Read this and carry out some computations during the laboratory class.

Heat is evolved by the hydrogen peroxide decomposition. This causes the temperature of the contents of the calorimeter (mainly water) to rise. The amount of heat given off by the decomposing hydrogen peroxide is equal to the amount of heat gained by the water (neglecting of course any heat that escaped from the calorimeter). The quantity of heat q gained by the solution in the calorimeter is given by:
$$q = (m) \, (s) \, (\Delta T)$$
where s is the specific heat of the solution, ΔT is the rise in temperature, and m is the mass of the solution. The formula $q = m \times s \times \Delta T$ is an important one to remember; it should be on your "must learn" list.

Since the solution in the calorimeter is mainly water, we make the simplifying assumption that its specific heat is identical to that of water, 4.18 J/g °C, and that its density is also that of water, 1.00 g/mL.

Now proceed as follows:
(1)   On the basis of the above, calculate q. (Recall that, at constant pressure, $q = \Delta H$.)

(2)   Find the heat evolved for 1 mole of H_2O_2. To do this, you will first need to work out how many grams of H_2O_2 were used. Remember that the solution contained 10% by mass H_2O_2.

(3)   Enter the appropriate values on the report sheet.
       The quantity of heat, q, evolved or absorbed in a reaction is related to the strengths of bonds broken and formed in the reaction. How well does the value you calculated from bond-strengths (question 1 on the report sheet) agree with the value you measured in this experiment?

Part II: Enthalpy of Hydration of Copper (II) Sulfate

Anhydrous copper (II) sulfate is colorless while the pentahydrate $CuSO_4 \cdot 5H_2O$ is blue. Heat must be supplied to drive off water from a hydrated salt. Conversely, if water is added to a "naked" cation or anion that is capable of hydration, then heat is evolved. In this experiment, you will measure the heat of hydration of anhydrous copper (II) sulfate, i.e. the heat evolved in the reaction

$$CuSO_4 (s) + 5\ H_2O\ (l) \rightarrow CuSO_4 \cdot 5H_2O\ (s)$$
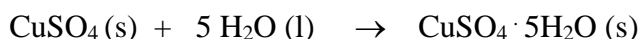
PROCEDURE:

1) Weigh a porcelain dish empty.
2) Add to it approximately 5.0 g Of $CuSO_4 \cdot 5H_2O$, and reweigh the dish to find out exactly how much you added.
3) Using your laboratory burner, heat the porcelain dish with contents to drive off the water of hydration. Periodically, remove the dish from the flame with tongs and break up solid lumps Of $CuSO_4$ with a spatula. Avoid losing any solid.
4) Continue heating until all the copper(II) sulfate has been converted to the white anhydrous powder.
5) Allow the dish to cool. Grind up any lumps that may be present. Re-weigh.
6) Place the anhydrous copper (II) sulfate into a dry calorimeter and cover it.
7) Measure to the nearest 0. 1 $^{\circ}C$ the temperature of 25.0 mL of water (contained in a graduated cylinder), then add this water quickly to the calorimeter containing the anhydrous $CuSO_4$.
8) Stir the calorimeter well for about a minute to ensure that all the copper sulfate has dissolved.
9) Measure the temperature of the calorimeter contents.

We also need to measure the heat change when blue crystals of $CuSO_4 \cdot 5H_2O$ dissolve in water. The difference between the two heats of solution is the heat associated with the interaction of the first five water molecules with copper (II). This is done in a similar fashion to the above.

10) Weigh out about 5.0g of $CuSO_4 \cdot 5H_2O$ into a previously weighed dry calorimeter; reweigh to find the exact weight you added.
11) Carefully measure the temperature of 25 mL of water (estimate to the nearest 0.10), and then add the water quickly to the calorimeter.
12) Mix for about a minute, insert the thermometer, and measure the final temperature of the solution, again estimating to the nearest 0.10.   This time, the temperature change

resulting from the process is much smaller, and in fact, the temperature of the calorimeter contents actually decreases. We will take up this interesting phenomenon below.

13) Use the results obtained from steps (1) - (12) to calculate ΔH per mole for the process:

$$CuSO_4 (s) + 5 H_2O (l) \rightarrow CuSO_4 \bullet 5H_2O (s)$$
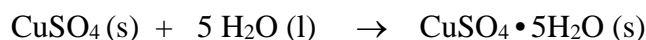
CALCULATIONS:

When we add 25 mL of water to anhydrous copper (II) sulfate, the result is a blue solution of the pentahydrate $CuSO_4 \cdot 5H_2O$.   It is useful to think of this overall process as taking place in two steps:
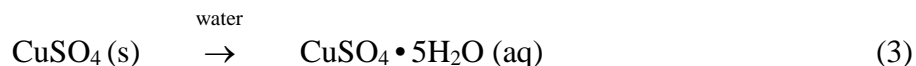
Step 1: Hydration of the solid anhydrous salt

$$CuSO_4 (s) + 5 H_2O (l) \rightarrow CuSO_4 \bullet 5H_2O (s) \qquad\qquad (1)$$

Step 2: Dissolution of the pentahydrate

$$CuSO_4 \cdot 5H_2O (s) \quad \xrightarrow{\text{water}} \quad CuSO_4 \bullet 5H_2O (aq) \qquad\qquad (2)$$
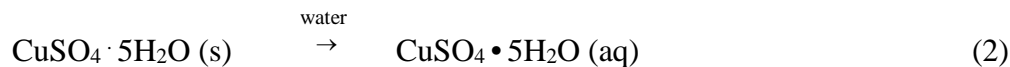
The heat released in the overall reaction (3) is then the sum of the enthalpies for reactions (1) and (2).   (i.e. $\Delta H_3 = \Delta H_1 + \Delta H_2$)

$$CuSO_4 (s) \quad \xrightarrow{\text{water}} \quad CuSO_4 \bullet 5H_2O (aq) \qquad\qquad (3)$$

Since you separately measured the heat changes for reactions (2) and (3), you can calculate the heat change for reaction (1). Enter all results and calculations on the Report Sheet.

Step III: The Enthalpy and Entropy of Dissolution of Ammonium Chloride

In Part 2, you were possibly surprised that when $CuSO_4 \bullet 5H_2O$ dissolves, the temperature of the solution drops. One of the early puzzles in science was to figure out why endothermic processes such as this occur at all, since we know that, in general, chemical systems, in common with other natural systems, have a tendency to achieve the state of lowest energy.

The puzzle was eventually solved. In addition to having a tendency to achieve lower energy, chemical systems (and other natural systems) have a tendency to achieve a greater degree of disorder (entropy). In the present case, these two fundamental tendencies oppose one another. In the dissolution process, the breaking up of the highly organized crystal lattice when salvation occurs results in greater randomness or disorder. This same process clearly results in an increase in energy upon going from reactants to products (we observe a temperature drop because the heat energy needed to drive the process is obtained from the water molecules that constitute the "surroundings", which therefore cool down). Since we observe that $CuSO_4 \bullet 5H_2O$ definitely does dissolve in water, we conclude that in this case the randomization effect is sufficiently great to offset the unfavorable requirement to supply heat energy. As stated in the Introduction, the condition for a process to occur (for it to be "spontaneous") is that

$$\Delta G < 0 \qquad\qquad (4)$$

where
$$\Delta G = \Delta H - T(\Delta S) \qquad\qquad (5)$$

Thus, even though the ΔH term is endothermic and therefore unfavorable, this may be offset by a sufficiently favorable (i.e. positive) ΔS to give a net ΔG which is negative and favorable.

In this part of the experiment, we will work with ammonium chloride crystals. When these crystals dissolve in water, the drop in temperature is quite large. This reaction is quite strongly endothermic, yet it occurs readily. Clearly the $T\Delta S$ term outweighs the ΔH term. We will measure ΔH and, keeping equations (4) and (5) in mind, we will calculate a lower limit to ΔS for this reaction.

PROCEDURE: **Complete 7-8 trials and report your average value and range based on standard deviation**.

(1)   Just for fun, give yourself a rough quantitative feel for the endothermicity of the dissolution of ammonium chloride. Place about 1 g of ammonium chloride crystals in a test tube, add a few mL of water, and feel the outside of the test tube. Isn't that cool? Now we will use the calorimeter to measure q, and hence ΔH_f^o this reaction.

(2)   Weigh about 5 g ammonium chloride into a previously weighed dry calorimeter; reweigh to find out how much you added.

(3)   Measure 25.0 mL of water (graduated cylinder) and record its temperature.

(4)   Pour the water quickly into the calorimeter.

(5)   Swirl the calorimeter contents for about a minute, then measure the temperature of the solution (nearest 0. 10)

(6)   Calculate ΔH -associated with the dissolution of a mole of NH_4CI.

(7)   Calculate the minimum possible value for ΔS for the dissolution of a mole of ammonium chloride. This would correspond to a $(-T\Delta S)$ term just sufficient to give $\Delta G=0$ when combined with the measured ΔH. What should you use for T?

Standard Deviation Review

The **standard deviation** of a series of measurements which includes at least 6 independent trials may be defined as follows. If we let x_m be a measured value, **N** be the number of measurements, $\langle x \rangle$ be the average or **mean** of all the measurements, then **d** is the **deviation** of a value from the average:

$$\mathbf{d} = \mathbf{x}_m - \langle \mathbf{x} \rangle$$

and the standard deviation, **s**, is defined by:

$$s = \sqrt{\frac{\Sigma d^2}{(N-1)}}$$

where $\Sigma \mathbf{d}^2$ means "sum of all the values of $\mathbf{d}^2$."

The **value of the measurement** should include some indication of the precision of the measurement. The standard deviation is used for this purpose if a large number of measurements of the same quantity is subject to random errors only. We can understand the meaning of **s** if we plot on the y-axis the number of times a given value of x_m is obtained, against the values, x_m, on the x-axis. The "normal distribution curve" is bell-shaped, with the most frequent value being the average value, $\langle x \rangle$.

Relative frequency of the occurrence of a measurement

68%

95%

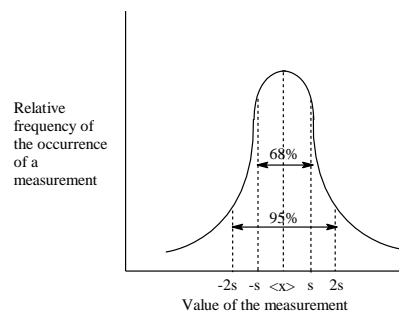-2s   -s $\langle x \rangle$ s   2s
Value of the measurement

Figure 1 : Distribution of values of a measurement

Most of the measurements give values near $\langle x \rangle$. In fact, 68% of the measurements fall within the standard deviation s of $\langle x \rangle$ (see graph). 95% of the measured values are found within $2s$ of $\langle x \rangle$. We call the value of $2s$ the uncertainty of the measurement, u. Then, if we report our value of the measurement as $\langle x \rangle \pm u$, we are saying that $\langle x \rangle$ is the most probable value and 95% of the measured values fall within this range. The next example shows how the standard deviation can be used to evaluate the data.

Example 1. Weight of a test tube on 10 different balances

Balance Number	Weight (g)=x_m	d=x_m-$\langle x \rangle$	d^2
1	24.29	0.00	0.0000
2	24.26	-0.03	0.0009
3	24.17	-0.12	0.0144
4	24.31	0.02	0.0004
5	24.28	-0.01	0.0001
6	24.19	-0.10	0.0100
7	24.33	0.04	0.0016
8	24.50	0.21	0.0441
9	24.30	0.01	0.0001
10	24.23	-0.06	0.0036
	Σx_m=242.86		Σd^2=0.0752

$$\langle x \rangle = 242.86/10 = 24.29 \, g \text{ and } s = \sqrt{(0.0752/9)} = 0.0917, \text{range} = \langle x \rangle \pm 2s = 24.29 \pm 0.18 \, g$$

or, the test tube weighs between 24.11 and 24.47 g, with 95% certainty.

Now each of the values of x_m are checked against the range. We observe that the weight from balance 8 is outside the range; we should discard it as unreliable and recalculate $\langle x \rangle$, d, d^2 and s.

The Q Test

For most of the experiments in this course, the standard deviation, s, is inappropriate to calculate because we perform too few measurements of the given quantity. When there are few measured values (<6), the **Q test** is used to decide whether to reject suspected "bad" values.

$$Q = \frac{|\,(\text{suspect value}) - (\text{nearest value})\,|}{|\,(\text{l arg est value}) - (\text{smallest value})\,|}$$

If Q for a set of data is larger than those listed in the table below, the suspect value may be rejected and the average of the other values is reported. (Note that the sign of Q is not important since we use the absolute value.)

Q test values for 3 to 5 measurements, 90% probability

N (# of measurements)	3	4	5
Q	0.94	0.76	0.64

Example II. The Q test

A student determines the molarity of a hydrochloric acid solution by titration with standard NaOH. He obtains the values 0.555, 0.565 and 0.564 M. Should the value 0.555 M be rejected, because the other two values are very close to each other? Apply the Q test:

$$Q = \frac{|\,0.555 - 0.562\,|}{|\,0.565 - 0.555\,|} = \frac{0.009}{0.010} = 0.90$$

Since 0.90 is less than the tabulated value of 0.94 for 3 measurements we may **not** reject the suspect value, 0.555. We report the average value $\langle x \rangle$ with the average deviation $\langle d \rangle$:

Value, x_m	d=$|x_m$-$\langle x \rangle|$
0.555	0.006
0.565	0.004
0.564	0.003
Σx_m=1.684	Σd=0.013
$\langle x \rangle$=0.561	$\langle d \rangle$=0.004

If agreement is bad, the chemist will repeat the measurement until he is satisfied.

NAME_____   SECTION _____
REPORT SHEET   EXPERIMENT 9

Enthalpy Measurement in Chemical Reactions

Part I: Hydrogen Peroxide Decomposition
1.   The heat evolved in a reaction is a reflection of the strengths of the bonds broken and formed in the reaction. For every bond that is broken, energy is required, while for every bond that is formed, there is a release of energy. ΔH values can thus be used to evaluate bond strengths, and bond strengths can be used to estimate ΔH values. Find the bond energies for the substances listed below in your textbook and record those values in the table below. Now determine ΔH per mole for the decomposition of hydrogen peroxide using those values
.   The calculation should be done in your notebook.

Bond	Bond Energy (kJ/mol)
O-H	
O-O (of hydrogen peroxide)	
O-O (of molecular oxygen)	

2. Show all calculations in your notebook.

Initial temperature of 10% H_2O_2 solution   _____

Final temperature of reaction product (H_2O)   _____

Temperature increase   _____

Volume of solution   _____

Heat evolved (q) by reaction (show calculation)   _____

Number of moles of H_2O_2 decomposed (show calculation)   _____

ΔH/mole of H_2O_2 decomposed   _____

ΔH/mole of H_2O_2 calculated from bond energies   _____

Compare your experimental and calculated values of ΔH.

Part II: Enthalpy of Hydration of Copper (II) Sulfate

A. Enthalpy change for reaction: $CuSO_4$ (s) $+ 5H_2O$ (l) $\rightarrow CuSO_4 \cdot 5H_2O$ (aq)

Mass of $CuSO_4 \cdot 5H_2O$ heated   _____

Number of moles of $CuSO_4 \cdot 5H_2O$ _____

Number of moles $CuSO_4$ produced   _____

Initial temperature of 25 mL H_2O _____

Final temperature of solution   _____

Change in temperature   _____

Heat evolved (q) by reaction (absorbed by solution)   _____

ΔH/mole for the reaction above: _____

B. Enthalpy change for reaction: $CuSO_4 \cdot 5H_2O$ (s) + water $\rightarrow CuSO_4 \cdot 5H_2O$ (aq)

Mass of $CuSO_4 \cdot 5H_2O$ _____

Number of moles of $CuSO_4 \cdot 5H_2O$ _____

Initial temperature of 25 mL H_2O _____

Final temperature of solution   _____

Change in temperature   _____

Heat absorbed by reaction (q) (lost from solution)   _____

ΔH/mole for the reaction above: _____

C. Enthalpy change for the reaction: $CuSO_4$ (s) $+ 5 H_2O$ (l) $\rightarrow CuSO_4 \cdot 5H_2O$ (s)
   Calculate the enthalpy change for the above equation (equation (3)), remember that
   $\Delta H_3 = \Delta H_1 + \Delta H_2$.

Part III: The Enthalpy and Entropy of Dissolution of AmmoniumChloride

1.   Show all calculations and trials in your notebook. Give a sample trial on this sheet.

Mass of ammonium chloride (for mole calculation)   _____

Number of moles of ammonium chloride   _____

Initial temperature of 25 mL water   _____

Final temperature of solution   _____

Heat absorbed from surroundings (by the solution)   _____

ΔH/mole for the dissolution   _____

Average ΔH/mole for the dissolution and range   _____

Show your calculation of the standard deviation, **s**, from $\mathbf{d}^2$ below:

Minimum average ΔS value for this reaction   _____

2.   When hydrogen peroxide decomposes (Part 1 of the experiment), the temperature rises. A fellow student argues that this means that heat must be taken in from the surroundings rather than heat being evolved to the surroundings. The same student of course wants to believe that when ammonium chloride dissolves (Part 3) and the temperature decreases, this is because heat is "lost" or evolved to the surroundings, causing the measured temperature to drop.   In your notebook write, as clearly as you can, a rebuttal of this false "logic". Do not forget good English and organizational skills, as well as your understanding of the issues.