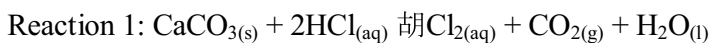Determination of the Enthalpy Change of a Reaction

Determine the enthalpy change of the thermal decomposition of calcium carbonate by an indirect method based on Hess' law.

Using the proposed method of obtaining results, these values were gathered:

Reaction 1: $CaCO_{3(s)} + 2HCl_{(aq)}$ 胡$Cl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

Experiment Number	Mass of CaCO3 (g)	Temperature Change (Δ)
1	2.50	2
2	2.55	2 1/6
3	2.50	2 1/4
4	2.53	2 1/6
5	2.47	2
μ	**2.51**	**2.12**

Reaction 2: $CaO_{(s)} + 2HCl_{(aq)}$ 胡$Cl_{2(aq)} + H_2O_{(l)}$

Experiment Number	Mass of CaO (g)	Temperature Change (^{o}K)
1	1.30	9 1/2
2	1.36	10 1/3
3	1.46	11
4	1.35	10 1/6
5	1.40	10 1/2
μ	**1.37**	**10.3**

μ in both cases represents the mean of the data.

Using the equation for enthalpy change: $\mathbf{\Delta H = mc\Delta T}$

Where: m = Mass of liquid to which heat is transferred to (g)

c = Specific heat capacity of aqueous solution (taken as water = 4.18 J.g^{-1}.K^{-1})

ΔT = Temperature change (^{o}K)

We can thus determine the enthalpy changes of reaction 1 and reaction 2 using the mean (**μ**) of the data obtained.

Reaction 1: ΔH = 50 x 4.18 x -2.12

ΔH = -443.08

This value is for 2.51g of calcium carbonate, not 100.1g which is its molecular weight.

Therefore: ΔH = -443.08 x (100.1 / 2.51) = -17670.2 J.mol^{-1}.

ΔH = -17.67 kJ.mol^{-1}.

Reaction 2: ΔH = 50 x 4.18 x -10.3

ΔH = -2152.7

This value is for 1.37g of calcium oxide, not 56.1g which is its relative molecular mass.

Therefore: ΔH = -2152.7 x (56.1 / 1.37) = -88150.7 J.mol^{-1}.

ΔH = -88.15 kJ.mol^{-1}.

Hess' law states that: [1]"The total enthalpy change for a chemical reaction is independent of the route by which the reaction takes place, provided initial and final conditions are the same."

This means that therefore the enthalpy change of a reaction can be measured by the calculation of 2 other reactions which relate directly to the reactants used in the first reaction and provided the same reaction conditions are used, the results will not be affected.

We have the problem set by the experiment: to determine the enthalpy change of the thermal decomposition of calcium carbonate. This is difficult because we cannot accurately measure how much thermal energy is taken from the surroundings and provided via thermal energy from a Bunsen flame into the reactants, due to its endothermic nature. Therefore using the enthalpy changes obtained in reaction 1 and reaction 2 we can set up a Hess cycle:
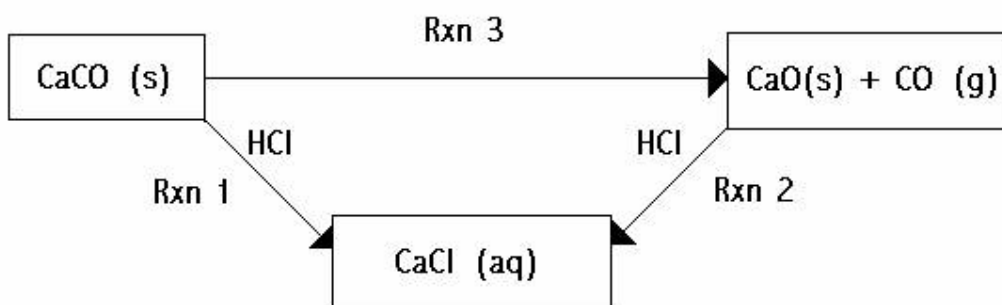
Thus using Hess' law we can calculate the enthalpy change of reaction 3.

Reaction 3: ΔH = Reaction 1 - Reaction 2

ΔH = -17.67 - (-88.15) = +70.48 kJ.mol^{-1}.

Comparing the value +70.48 kJ.mol^{-1} to the theoretical value of this enthalpy change (101kPa, 298K): +177.8 kJ.mol^{-1}, there is a huge difference.

Percentage error is calculated by:

100 x <u>Theoretical Value - Actual Value</u>

Theoretical Value

Percentage error = (177.8 - 70.48) / 177.8 = **60.4%**

Considering the scatter diagrams, they show the expected positive correlation. This is, the more reagents added, the more products there are. The amount of products formed is directly proportional to the temperature change since this is the amount of energy transferred as a result of the breaking and forming of intra-molecular bonds.

The scatter diagrams at first glance look as if they follow different gradients, however considering the scales upon which the results in either diagram is measured, it shows they both increase at the same rate represented by a positive linear relationship.

This can described in the form $y = mx$, m being the gradient of the rate of temperature increase in respect to mass of reagents present.

Standard deviation will give us an indication as to the accuracy of the results.

	Variance (σ^2)	Standard Deviation (σ)
Reaction 1	7.6×10^{-4}	2.76×10^{-2}
Reaction 2	2.88×10^{-3}	5.37×10^{-2}

However these very small standard deviations show us that all results are very closely distributed and inaccuracy in this experiment could have been slightly contributed from this source, but to no great degree.

In conclusion, considering the data collected is of very low standard deviations, it must be that the method of obtaining enthalpy changes is of great inaccuracy.

However the data demonstrates that there is potential for accuracy in this method due to their small standard deviations and with much revision the method could provide much more limited error margins which could provide enthalpy changes which more closely resemble theoretical data.

What factors could affect our calculated enthalpy change so much as to produce such a percentage of error?

The reaction was conducted in a simple laboratory environment, where achieving standard conditions of 298K and 101kPa were not practical both in terms of time of the procedure and economics of achieving such precise conditions. Therefore comparing our calculated value of +70.48 kJ.mol^{-1} to the theoretical value written in a book of data: +177.8 kJ.mol^{-1}; a quite substantial error could be produced. Since the reactions were exothermic and temperature and pressure may have been higher than standard conditions, this could have provided a shift in the equilibrium to the endothermic direction, thus in accordance with Le Chatelier's Principle of equilibrium dynamics, less products were formed and a lower enthalpy calculated.

However, one of the main sources of error would have been the use of the lab thermometers which had small graduations and a large temperature range providing inaccurate methods in which to measure temperature changes. The basic thermometer comprises of a coloured liquid filled capillary tube which when heated increases in volume at such a degree to show the change in temperature proportional to the volume increase. When conducting experiments which are solely based around a change in temperature, the use of simple glass thermometers is not appropriate. However, a digital thermometer would show much more accurate temperature changes which are particularly vital when dealing with small temperature changes such in the instance of reaction 1. This would decrease the percentage error between actual and theoretical results of enthalpy change.

When measuring exothermic reactions as with reactions 1 and 2, it is important that when the reaction takes place, as little heat is lost to the environment as possible. This is even more important when dealing with temperatures that far exceed the environmental temperatures of the laboratory, since it means a steeper temperature gradient out of the system and therefore more thermal energy lost as a result.

In order to reduce heat lost, the method incorporated a polystyrene cup with a plastic lid which was meant to insulate the system from heat loss as best as possible. However, since the calcium carbonate and calcium oxide had to be introduced into the hydrochloric acid, it mean that the cup had to be unsealed via the plastic top which mean that heat was lost as a results before being sealed.

The plastic used for the top was thin and was a poor insulator. Since heat rises, it means that the plastic top had a greater effect on the loss of heat than the greater surface area of the sides and bottom of the system insulated by the polystyrene cup.

A system surrounded in a vacuum would have prevented the loss of heat entirely, reducing any error to an absolute minimum and producing very accurate sets of data.

Consider result on scatter diagram for reaction 1 with co-ordinates (2.5, 2.25). It does not fit into a line of best fit for the diagram by any means, so what factors within the experiment could have altered in order to produce such an anomaly?

Firstly, it is above a line of best fit which means it caused a relatively substantial temperature change upon the solution for the mass of the calcium carbonate reacted.

This could have been because the mass of calcium carbonate was weighed incorrectly, but taking into account that the scales use were digital, any inaccuracies are highly unlikely.

Possibly the mass of calcium carbonate was a large lump and therefore had a smaller surface area: volume ratio and so when it was introduced to the hydrochloric acid it reacted more slowly. Thus, less thermal energy was lost in the time before the plastic top was sealed in place and more thermal energy was provided to the system creating a greater temperature change.

When adding the calcium carbonate to the solution of hydrochloric acid, the solution effervesces and therefore there is a lesser volume of liquid to transfer thermal energy

to and a greater change in temperature as a result. However, the volume of solution transferred in this way is negligible and therefore the overall effect is almost insignificant in comparison.

Using the equation to calculate enthalpy change of a reaction: $\mathbf{\Delta H = mc\Delta T}$.

There are various assumptions associated with this calculation which makes it slightly crude as a true representation of the enthalpy change of a reaction. These are that the specific heat capacity of all solutions to which a temperature change has occurred is taken as the value for water. This is relatively high due to its high stability from its hydrogen bonding. Therefore with solutions with a lower specific heat capacity, less thermal energy is required to raise the temperature of the solution and the enthalpy change is not as great as suspected.

Also the density of the solution is judged as water which has a density of 1. That is, for every 1 cm^3 of liquid, it has a mass of 1 gram. This is because Density = Mass / Volume.

However, no solutions have a density of 1 unless of course they are pure water. This means that there could, in fact be a larger amount of molecules to which the thermal energy is transferred to. Therefore with solutions with greater density, more thermal energy is required to raise the temperature of the solution and the enthalpy change is greater than suspected.

Taking into account all of these potential areas of limitation of the method, if the experiment were to be repeated, it would have to include as many methods in which to prevent these sources of error to occur. This would include: conducting the experiment in a vacuum flask, using a digital thermometer to display an exact change in temperature of the solution, the flask to contain a method of introducing the solid reagent without loss of heat, provide standard conditions under which to conduct the experiment and use the true specific heat capacity and density of hydrochloric acid when calculating enthalpy changes.

For $CaCO_3$: $T_1 = 17$

$T_2 = 19$

DT= 02

using 2.57g of $CaCO_3$

For CaO: $T_1 = 18$

$T_2 = 27$

DT= 09

using 1.39g of CaO

Analysis:

In order to determine the enthalpy change for the thermal decomposition of calcium carbonate, we must work out the enthalpy changes for both the reactions of calcium carbonate and calcium oxide with hydrochloric acid.

For $CaCO_3$:

Temperature change = 2?C

To find the enthalpy change of a reaction, we must first work out the amount of energy taken in by the reaction. This is done by using the following formula:

E=DT x mass surroundings x specific heat capacity of surroundings

For this calculation, we will assume that the specific heat capacity of HCl is identical to that of water, and that the shc of water is 4.2J/?C/g. We used 51cm^3 of HCl, so the mass of this is taken to be 51g, as 1cm^3 of water weighs 1g (and we are assuming that HCl(aq) has the same density as water). So, putting this data into the equation, we get:

E= (-2) x 51 x 4.2

= -428.4J

Then, in order to find the enthalpy change for this reaction, this value should be converted into kJ, and divided by the number of moles of the substance (in this case, calcium carbonate). To find the number of moles used, we divide the mass used by the relative atomic mass of the substance. So, we get:

N^o moles = Mass ?M_r

= 2.57 ?100.08

= 0.026 mol.

Then we convert our energy into kJ rather than joules, getting 0.4284 kJ, and dividing this by the amount of substance we used. So, this comes out as:

DH= (E ? 1000) ? Nº moles

= (-428.4 ?1000) ?0.026

= -0.4284 ?0.026

= -16.4769

? -16 kJ mol^{-1}

For CaO:

Temperature change = 9?C

We have to follow exactly the same process and calculations as with calcium carbonate, only we used a different amount of CaO, and the temperature change was different.

So, using the formula

E=DT x mass surroundings x specific heat capacity of surroundings

We get:

E= (-9) x 51 x 4.2

= -1927.8J

Then, finding amount of CaO we used, we use the following formula:

Nº moles = Mass ?M$_r$

Getting:

Nº moles = 1.39 ?56.08

= 0.025 mol.

Then, having converted the energy intake into kJ (-1.9278 kJ), we put the data into this formula:

DH= (E ? 1000) ? Nº moles

Getting:

DH = (-1927.8 ? 1000) ?0.025

= -1.9278 ?0.025

= -77.112

? -77 kJ mol^{-1}

Now we have found both measured enthalpy changes, we can work out the enthalpy change for the thermal decomposition of calcium carbonate. This is done by following Hess's Law, which states that "The enthalpy change in a reaction is the same, independent of the number of steps taken, provided the reactants and products end up in the same states that they would ordinarily be". It is this principle that is behind this experiment - since we are dissolving both chemicals in HCl, and starting with solid calcium carbonate, calcium oxide and carbon dioxide, we can work out the enthalpy change using this law. This is best done by constructing a triangle, as shown below:

$\longrightarrow$ CaCO$_3$ DH$_3$ CaO + CO$_2$
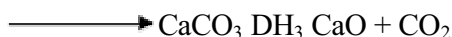
DH$_1$ DH$_2$

CaCl$_2$

We draw out the triangle, and can see that, in order to get from calcium carbonate to calcium oxide, we must go in the same direction as the DH$_1$ arrow, and against the direction of the DH$_2$ arrow. This means that DH$_3$ = DH$_1$- DH$_2$

So, substituting in our values for those of DH$_1$ and DH$_2$, we get:

DH$_3$ = DH$_1$- DH$_2$

DH$_3$ = -16 + 77

DH$_3$ = +61 kJ mol^{-1}

According to the experimentally determined values, DH for the thermal decomposition of Calcium carbonate is +61 kJ mol^{-1}.

Evaluation:

There were a large number of problems with this experiment, the most significant source of error being the heat loss to the apparatus. The reactions took place in a glass beaker. Glass has a relatively high heat capacity, and so a large amount of heat which

is either taken in or given out is lost to the apparatus. This is obviously a major problem, especially with the reaction of calcium carbonate with HCl, as this does not appear to have a very large change in temperature, so every slight bit of absorption by the apparatus will have a large effect on the temperature change, and consequently the enthalpy change. Th other piece of apparatus that will have absorbed a lot of heat is the thermometer itself, as it is also made of glass, and so also has a high heat capacity, leading to similar problems as with the beaker. Another inaccuracy in the experiment was the time at which the temperature was taken - it was taken at the end of the reaction, which will have resulted in a temperature change which will have been less than it should have been. This can be counteracted by taking the peak temperature reached. The problem of heat loss to the apparatus could also be reduced by performing the experiment in an insulating container - for example; a polystyrene cup would dramatically reduce the amount of heat lost. As I mentioned above, apart from the beaker, the thermometer itself also absorbs a large amount of the thermal energy. This could be avoided by using a temperature-measuring device (such as a thermistor) with a low heat capacity, so that minimal heat is lost to it. Another major problem of the experiment would be the heat that is lost not to the apparatus, but to the surroundings. This is a problem, as it means that the reading on the thermometer even if it did have a low heat capacity, would still not be the same as the actual change, as some is lost to the surroundings. We also had a major problem with the time at which the temperature was taken - we were instructed to take the temperature at the end of the reaction, by which time it had fallen significantly as the solution had cooled whilst the last remnants of the reaction were taking place. A way to prevent this would be to take the peak temperature on the thermometer, as this is the maximum measurable value, so must be the maximum measurable enthalpy change. There was yet another problem with the scale of the thermometer - we were using 0-100?C thermometers to measure relatively small changes - 2?C for calcium carbonate. This is a problem, as it is harder to read off accurately the temperature change when using a big scale and experiencing a small change - there is a large possible percentage error. This obviously has a large impact on our calculations, as the temperature change must be recorded as accurately as possible in order to get a correct representation of the enthalpy change. A method of combating this would be to use a 0-50?C thermometer, as this has smaller gradations on it, and so it is easier to read off the values. It may be even better to use a digital thermometer, which has been professionally calibrated to a high degree of accuracy - this minimises the human error in taking a reading from the thermometer.

There were also a number of other problems with the experiment, but these were of lower significance than those mentioned above. The most easily noticed one of these is the measuring cylinder - we were instructed to use a $250cm^3$ measuring cylinder to measure out $50cm^3$ of 2 mol dm^{-3} HCl. This could have produced an error, as it is using a large cylinder to measure out a relatively small amount of acid. However, whilst meaning that this variable was not entirely under control during the experiment, as the acid was in excess, it is not especially crucial that exactly $50cm^3$ was used - it does not affect the readings taken. Another variable was the concentration of the acid. This could have affected the results, by the concentration not being accurate. If this were the case, however, then the error would have been systematic, and so will have appeared in both sets of results, as the acid was drawn from the same bottle. Another one of these small errors is the accuracy of the balances - the readings given may not have been entirely accurate. However, this slight

inaccuracy (?0.004g) pales in the face of the other experimental problems, so it can be safely disregarded.

These problems were not the only ones with the experiment - the major factor being that it was only performed once, with no repeats - these values were taken to be correct, with no comparisons made. This could easily be rectified by performing a suitable number of repetitions - for example, 4 repetitions could be made, and an average taken. This would vastly improve the reliability of the end results, as the average would more accurately reflect the true temperature change.

Overall, there were a large number of problems with this experiment, and correspondingly, there are a large number of things that I would like to change if I were to be able to repeat this experiment. The experiment was successful I that results were obtained, but I suspect that these results are vastly different to the actual values.