EXPERIMENT IX

KINETICS OF DECOMPOSITION OF SODIUM BICARBONATE; A DIFFERENTIAL SCANNING CALORIMETRY EXPERIMENT

1. Purpose

Upon heating, sodium bicarbonate decomposes into water, carbon dioxide and sodium carbonate according to the main reaction:

$$NaHCO_3 \rightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}H_2O + \frac{1}{2}CO_2 \tag{1}$$

The technique of differential scanning calorimetry will be used to measure the enthalpy of decomposition for this process; in addition, kinetic information relevant to reaction (1) may be obtained from an analysis of the DSC data collected at different temperature scanning rates.

2. Safety

Although the chemicals (small amount of indium and sodium carbonate) used in this experiment are not particularly hazardous, please wear your safety goggles at all times; there are many potentially hazardous chemicals or pieces of equipment present in the lab.

3. Introduction

Calorimetric measurements in general provide quantitative information on the amount of energy evolved during a chemical or physical process. In the technique of Differential Scanning Calorimetry (DSC), energy absorbed or evolved by the sample due to some physical or chemical process is compensated by adding or subtracting an equivalent amount of electrical energy to a heater located in the sample holder. The calorimeter is programmed to scan the temperature at a linear rate. The continuous and automatic adjustment of heater power (energy per unit time) necessary to keep the sample holder temperature identical to that of a reference holder provides a varying electrical signal equivalent to the thermal behaviour of the sample. This measurement is made directly in energy units (mW), providing true electrical energy measurement of peak areas. As long as no reaction or no physical change occurs in the sample, this differential in energy stays constant (or varies slowly). When a reaction occurs, the change in heat content and in the thermal properties of the sample are manifested by a sudden change in the amount of electrical power required to keep the temperature of the sample pan equal to that of the reference pan; less power would be needed if an exothermic process were to occur while excess power would be required for an endothermic process. This differential flow of energy is recorded as a deflection from the baseline or a "peak" (positive deflection for endothermic process, negative deflection for exothermic process). One can show [2] that the area under the "peak" is directly proportional to the enthalpy of the process under investigation.

If one is dealing with an activated process (i.e., there is an activation energy), the reaction rate varies with temperature; in other words, the rate of reaction is constantly changing as the temperature scan progresses and consequently the position of the "DSC peak" will depend on the temperature scanning rate providing that other experimental conditions are kept constant. It can be shown [1] that the activation energy is related to the position of the peak and the scanning rate. In short, three types of information can be extracted from a series of DSC scans: any deflection from the baseline indicates some change in the physical or chemical properties of the sample, the area under the peak is related to the heat of the reaction while the shift in peak position as a function of temperature scan rate is related to the activation parameters of the reaction. In addition, for the particular case of decomposition reaction, the peak shape is related in a simple way to the order of the reaction [1].

3.1 TEMPERATURE OF MAXIMUM DEFLECTION

Simple decomposition reactions of the type

$$Solid \rightarrow Solid + Gas \tag{2}$$

have been shown[1] to obey the rate law

$$\frac{dx}{dt} = A(1-x)^n e^{\frac{-E^*}{RT}} \tag{3}$$

where A and E^* are the Arrhenius parameters, dx/dt the reaction rate and x the fraction reacted; n is the empirical order of the reaction. Assuming that n stays constant throughout the extent of the reaction and that the heating rate is constant, after some simplification one gets the approximate expression, independent of reaction order:

$$\frac{d\left(\ln\frac{\phi}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} \approx \frac{-E^*}{R} \tag{4}$$

$$\text{Or } \ln\frac{\phi}{T_m^2} \approx \frac{-E^*}{R}\frac{1}{T_m} + \text{constant} \tag{5}$$

where T_m is the peak temperature (temperature of maximum deflection) of the differential scan corresponding to the heating rate ϕ. Eqn. (5) shows that the activation energy for reaction (2) may be obtained from the slope of a plot of $\ln(\phi/T_m^2)$ against $1/T_m$.

3.2 REACTION ORDER AND PEAK SHAPE

As mentioned earlier, the heating scan rate affect the shape of the peak due to the fact that the reaction rate changes during the scan. In particular [1], the thermal analysis peak becomes increasingly asymmetrical as the reaction order *n* decreases. This effect is illustrated in Fig. 1 where the shape of several DSC peaks have been simulated for different reaction order (other things being equal).

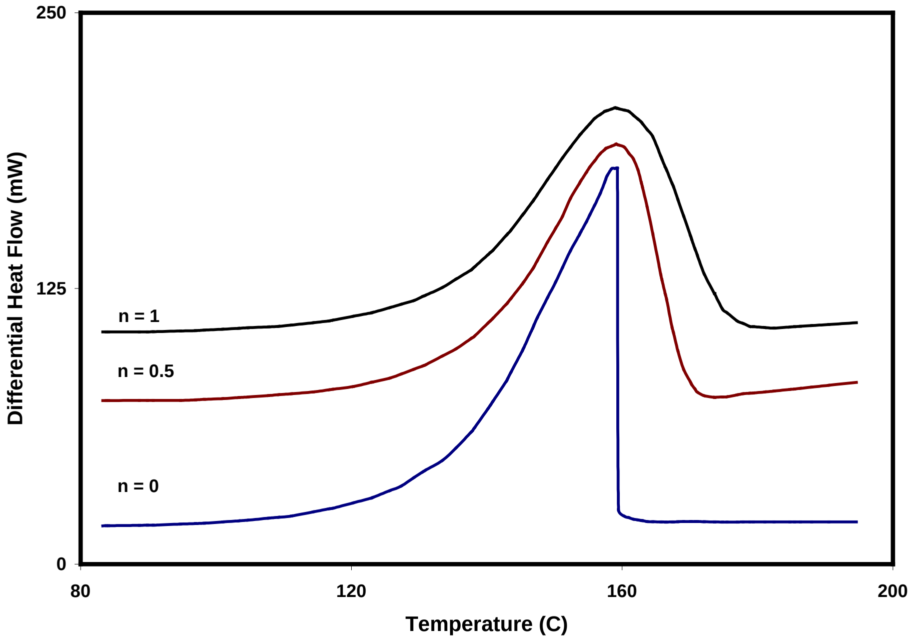

Figure 1. Effect of the reaction order on the DSC peak shape for constant heating rate and activation parameters; the curves shown are simulated DSC scans.

One can quantify the degree of asymmetry of the thermal analysis peak by defining the "shape index"

$$S = \frac{a}{b} \tag{6}$$

where the lengths *a* and *b* are defined in Fig. 2. According to this definition $0 \le S \le 1$ with $S = 0$ for a pure zeroth order reaction (most asymmetric shape) and $S = 1$ for perfectly symmetrical peak shape. Providing that the order of the reaction stays constant for most of the duration of the reaction, one finds that to a good approximation the shape index *S* as defined in Eq. (6) is a function only of the reaction order and obeys the empirical relationship:

$$S = 0.63\, n^2 \tag{7}$$

from which, in turn, the reaction order can be estimated

$$n = 126\sqrt{S} \tag{8}$$

4. Experimental.

The Differential Scanning Calorimeter used for the present experiment is a Perkin–Elmer DSC 7^{TM}. The apparatus consists of the DSC 7 unit itself and the TAC 7/DX controller unit, the whole thing being controlled by an IBM–DOS computer via a proprietary software.

3.1 START UP.

The following instructions are also found in a folder next to the machine.

Before powering up the different units, fill up the tank of the DSC 7 unit with ice/water and adjust if necessary the flow of the purging nitrogen to a few bubbles a second. To power up the system, turn the computer **`on`** and follow the instructions appearing on the screen (if the various units are not powered in the order indicated, communication between the computer and the apparatus may not be properly established). Hit the **`F1`** key to go to **`Set Up Menu`** or the **`F2`** key to go to **`Analysis Menu`**

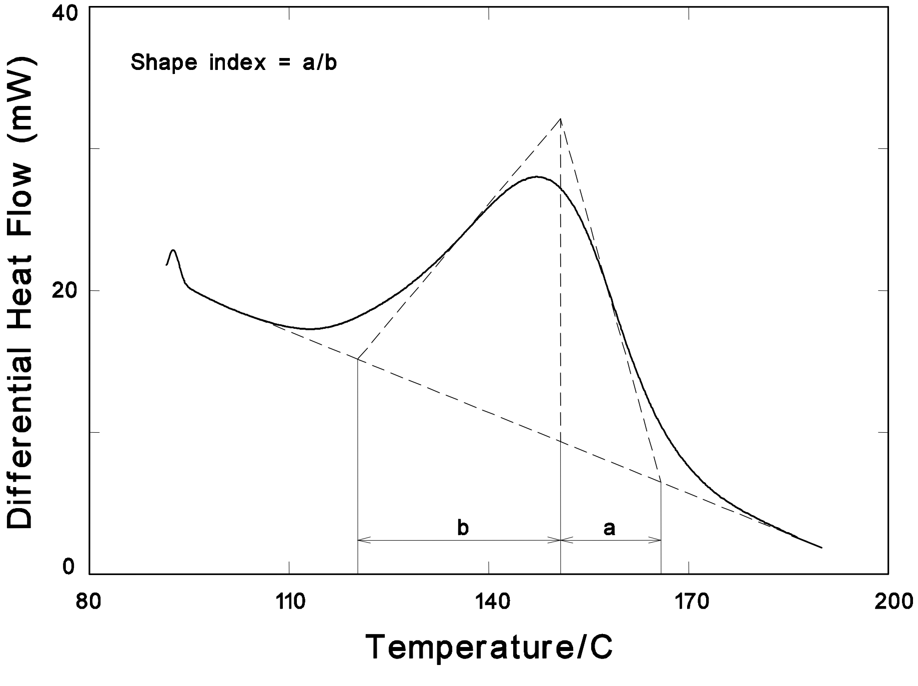

Figure 2. Method for quantifying the degree of asymmetry of a DSC peak. Distances a and b are the vertical projection on the peak effective baseline of the segments shown, which are the tangents at the inflection points of the rising and falling part of the peak.

3.2 SAMPLE PREPARATION.

All samples have to be first encapsulated into special aluminium pans using the specialized crimping tool provided; the instructor will show you how to perform this step.

All the following manipulations require a steady hand; DO NOT RUSH!

3.2.1 Indium Test Sample

To help familiarize yourself with the operation of the DSC apparatus, an indium sample is provided. Perform at least one DSC scan on this sample in the temperature range 120–180 C with a setting of 20 C min^{-1}. Since there is no decomposition of the sample, the temperature scan may be repeated many times with the same sample. Check that the melting point and the heat of melting as determined by the peak area agree with accepted values[1] (onset temperature 156.60 C, transition energy 28.45 J g^{-1}).

3.2.2 $NaHCO_3$ Samples.

A minimum of five samples of $NaHCO_3$ needs to be prepared. You can prepare a sample and run a DSC immediately or prepare all the samples first then run the DSC's one after the other. If you choose the second option, make sure that you have a mean of identifying each encapsulated sample. Since one is dealing with a decomposition reaction, a new sample is needed for each run. The weight of the sample should be in the range 3 to 10 mg measured precisely on the analytical balance.

3.3 SCANNING PROCEDURES.

>>>>>> WARNING <<<<<<

THE PAN ASSEMBLY IS DELICATE AND EXPENSIVE.

If anything falls into the gaps around the sample pan, do NOT attempt to retrieve it yourself; immediately switch all power `off` *on the DSC 7 unit and notify the instructor.*

3.3.1 Sample Loading.

- Lift the insulating draft shield and open the sample holder enclosure by lifting the latch and swinging open sideways the enclosure cover.
- Note which pan is used for sample; do not touch the other pan (the reference pan) which contains an empty aluminium pan. Using tweezers, lift the platinum

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[1] If the melting point and/or the heat of melting do not agree with the accepted values, all the temperatures and the peak areas obtained during the experiment will have to be corrected appropriately using the data from the indium run. Correct the temperatures by adding algebraically the offset observed between the accepted and the measured melting point. Peak areas are corrected by multiplying the area by the ratio of the accepted to the measured heat of melting.

cover, place the encapsulated sample, put the platinum cover back, shut and lock the sample holder enclosure, and finally replace the draft shield.

3.3.2 SetUp Parameters.

Once in the **`SetUp`** menu the **`F`** keys (1 to 10) are the "hot" keys and their respective meaning is displayed on the screen.

- * Select **`Parameters`** (**`F1`** key) menu item. The program parameters are displayed on the screen with their current values; a cursor points to the active parameter. To change the value of the active parameter, just enter the desired value and press **`Enter`**. If no change, press **`Enter`** to move the cursor to the next parameter. The **`up`** and **`down`** arrow keys may be also used to point to and edit the various parameters. The **`Esc`** key will cause an exit from this menu. If a value entered for a parameter is not acceptable, the message "Value out of range" will appear on the screen. Table 1 show typical values for the different scans to be performed. (*Note: as indicated in Table 1, run first the 2.5 °C min^{-1} scan; this will take some 40 min. Other samples can be prepared while this slow scan is running*).

Table 1. Recommended values for DSC **`Parameters`**.

	Indium	$NaHCO_3$				
T Final/°C	180.0	190.0	230.0	220.0	210.0	200.0
T Start/°C	120.0	90.0	80.0	80.0	90.0	90.0
Scan Rate/°C min^{-1}	**20.0**	**2.5**	**40.0**	**20.0**	**10.0**	**5.0**
Y Range/mW	50	50	50	50	50	50
Sample weight/mg			*as applicable*			
Baseline Status:	N	N	N	N	N	N
Multitasking:	N	N	N	N	N	N
Scan duration/min	*3*	*40*	*4*	*7*	*12*	*20*

- * Select **`Conditions`** (**`F2`** key) from the menu. The set of parameters in this menu controls the state of the DSC analyser when starting a run, during and at the end of a scan. For a given set of samples, the **`Conditions`** parameters are unlikely to be changed (for more details on the precise meaning of these parameters, consult the DSC 7 manual, p. 9-6). Enter the values for the various **`Conditions`** in the same fashion as in the previous section; the recommended values are shown in Table 2.
- * Select **`Id Sample`** (**`F3`** key) and fill in the screen requests.
- * You can verify the status of the current run parameters by selecting **`View Parameters`** (**`F7`** key); press **`Enter`** to clear the screen. To change any of the value displayed, go back to the main menu and select the appropriate sub-menu (see above).

The system is now ready to collect data.

3.3.3 Data Collection.

Check that the sample holder enclosure is closed and locked, and that the draft shield cover is in place (see above).

* Select **`Begin run`** (**`F6`** key); the analyser will heat to *T start* as selected according to Table 1 and data acquisition will begin after a delay of *Data delay* minutes into the run (0.3 min in the present case if the parameters were set according to Table 2). The progress of the scan is displayed on the screen. When the scan is over, select **`Save data`** (**`F8`** key) to store the data; use a different filename for each run.

* Repeat the whole procedure with each new sample.

When the last DSC run has been completed, do not forget to remove your last sample from the pan and to return the analyser to its original state. Also remove the pens from the plotter and put the pen caps back on (to prevent the pens from drying up).

Table 2. Recommended values for DSC **`Conditions`**.

End Condition:	L
Load Temp:	50.00
Go to Temp Rate:	200.0
Event 1 Time:	0.00
Event 2 Time:	0.00
Data Delay:	0.30
Time at T Start:	0.00
Time at T Final:	1.00
Y Initial Value:	10.00

5. Data Analysis

As mentioned in the Introduction, process your data in order to obtain,

a) the enthalpy of decomposition from the DSC peak area,

b) the Arrhenius activation energy from a plot of $\ln(\phi/T_m^2)$ versus $1/T_m$ (T_m in Kelvin please! And note that the temperature scanning rate ϕ is a differential quantity and consequently has the same value whether expressed in Celsius or Kelvin),

c) the empirical order of the reaction from the peak shape index.

The PE analysis software available on the computer attached to the DSC is most suited to get a). From the Main Menu, hit **`F3 Analyse Data`**, then **`F1 Peak`**. Next, one has to define a temperature window which frames the peak of interest. Using the side arrows keys, move the cursor to the left side of the peak, touch the **`Home`** key to activate the right cursor and again using the side arrows, move the right cursor to the right of the peak (one can go back to the left cursor by touching again the **`Home`** key), then hit **`Enter`** to accept the temperature window just defined. The results will be displayed on the screen. One can have these results "written" on the plotter; hit **`F5 Results`**, then **`Y`** (for yes). An actual plot of the DSC curve may be obtained on the same piece of paper on which the results were written. Hit **`ESC`** to go back to the **`Data Analysis Main Menu`**, the **`F5 Plot Options`** finally **`F1 Plot Screen`**. Alternatively, data may be exported and viewed using a spreadsheet, `DSC_results.XLS.`

For items b) and c), the necessary information may be extracted graphically from a plot of the DSC run, generated from the **`Analysis Menu`** on the Graphic Plotter.

Apply to your data the appropriate temperature and peak area correction using your indium run as a calibration run; if the melting point and/or the heat of melting do not agree with the accepted values, correct the temperatures by adding algebraically the offset observed between the accepted and the measured melting point. Peak areas are corrected by multiplying the area by the ratio of the accepted to the measured heat of melting.

Knowing that the heat of reaction (J/g) is calculated by the DSC software simply by dividing the measured peak area by the sample weight, which is provided by the operator as one of the run parameters, one can estimate the error on this heat of reaction reported by the instrument.

There is an EXCEL file (`DCSANAL.XLS`) designed to facilitate somewhat the analysis; you may copy it from one of the PCHEM computers (or download this file from *http://www.sfu.ca/~brodovit/files/chem366*). If you want to use this spreadsheet, you will need to make a copy of the data files corresponding to your DSC experiment (email or other appropriate data storage device). The data are stored on the hard disk in the directory `C:\PE\DATA` and the name of the corresponding files is `*filename*.D7`.

Warning. If the data is a bit noisy, the spreadsheet results may be erroneous; check on the plot generated by the Excel template whether the tangents at the inflection points of the DSC curve are sensible.

When handing in your report, submit at the same time your data tabulated in the spreadsheet `DSC_results.XLS` (which may be downloaded from *www.sfu.ca/~brodovit/files/chem366*)

6. Discussion

Discuss your results in light of reference[1].

What is the effect of the scan rate on the measured enthalpy of decomposition and the measured reaction order? Is an effect expected? Compare this result with the heat of decomposition calculated from the heat of formation of the individual compounds; comment on the agreement (or discrepancy). Are there features in your DSC scans which may be relevant to this discussion?

The sodium carbonate product, Na_2CO_3 has several hydrated form, each with a different heat of formation; again using literature heat of formation of individual starting compounds, calculate the heat of reaction corresponding to each possible hydrated product. From your results, which hydrate could be involved as a reaction product to explain the discrepancy between the heat of decomposition observed and the calculated one? If applicable, estimate the fractional contribution of this parallel reaction.

From your results, make some general recommendations as to the best scanning conditions when using the DSC technique. The DSC is one of the techniques used to characterize polymer samples. For these materials, what kind of information can be provided by this technique and why is it important?

7. References

[1] H.E. Kissinger, *Anal. Chem.* **29** (1957) 1702.

[2] *Perkin Elmer DSC7 Manual.*

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Chem 366W report check list

A report will not be accepted without all the items of this list checked. If a checked item is found missing in the report, the report will be automatically down-graded.

Student Name:____

Report: Differential Scanning Calorimetry

Title page.

Correct title of the experiment .... ☐
Student Name & student ID .... ☐
Partner name (*if applicable*)____
Date of performance of experiment .... ☐
Abstract .... ☐
Introduction and theory .... ☐
Experimental
Changes from text description mentioned (*if applicable*) .... ☐
Sample ID, ser no, stock solution …etc recorded (*if applicable*) .... ☐
Results
Results as Tables .... ☐
Graphs
 Size, at least ½ page .... ☐
 Axis labelled .... ☐
 Axis labels have units .... ☐
 Axis scales are sensible .... ☐
Only significant figures .... ☐
Uncertainties quoted .... ☐
Raw data provided (*electronic form, if applicable*) .... ☐
Calculations
Sample calculation provided .... ☐
Error analysis .... ☐
Sample error calculation provided .... ☐
Discussion
Comments on results .... ☐
Questions in text book and in manual answered .... ☐
Comparison with literature value(s) .... ☐
Conclusion .... ☐