Thermodynamics Experiment

The Enthalpy of H$_2$O$_2$ Decomposition in Aqueous Solution

OBJECTIVES

1. To illustrate the use of calorimetry in the experimental measurement of thermodynamic data.

2. To illustrate the use of thermodynamics and specifically Hess' Law calculation of enthalpies of reaction, using H$_2$O$_2$ decomposition as a model system.

INTRODUCTION

This experiment uses a calorimeter comprising a dewar vessel fitted with an electrically driven stirrer and a mercury thermometer. The calorimeter is well insulated from the surroundings. When an exothermic reaction is carried out inside the calorimeter, the temperature rises. Provided the reaction and associated temperature rise are rapid then correction for heat exchange between the calorimeter and the surroundings is unnecessary.

In a typical experiment the temperature inside the calorimeter is monitored for a period of five minutes. The reaction is then initiated, causing a temperature rise. The temperature inside the calorimeter is then monitored for a further five minutes.

A schematic temperature *vs* time graph is shown below. The readings are divided into two periods: pre-reaction and post-reaction. Ideally, during the pre-reaction and post-reaction periods the temperature should remain constant, but in practice there is often a slight drift owing to heat generated by the stirring and temperature equilibration between the calorimeter and its contents.

The pre- and post-reaction period readings should be linearly extrapolated to five and a half minutes. The difference $T_f - T_i$ then gives the correct temperature rise.
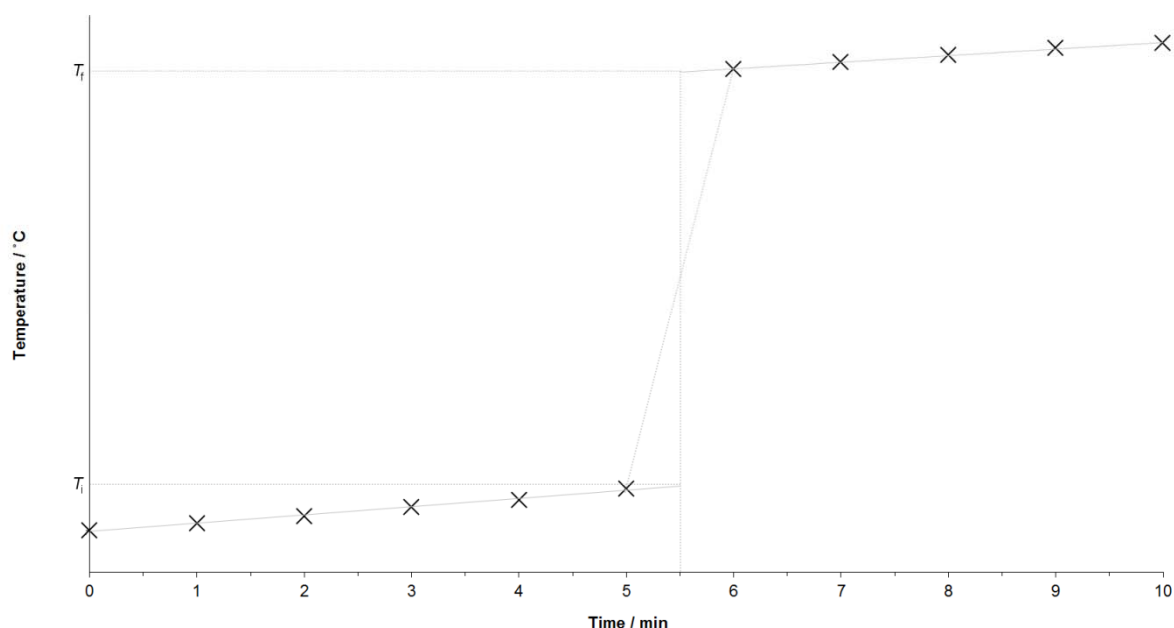
Figure 1: A schematic temperature *vs* time graph.

In this experiment a reaction of known molar enthalpy change is carried out inside the calorimeter. Measurement of the temperature rise enables determination of the heat capacity of the calorimeter. Then, A reaction of unknown molar enthalpy change is carried out inside the calorimeter. From the measured temperature rise and the known heat capacity of the calorimeter the unknown molar enthalpy may be calculated.

When an exothermic reaction is carried out in the calorimeter, the heat liberated by the reaction is not transferred from the calorimeter to the surroundings, but instead is used to heat up the calorimeter and its contents. If the temperature increase is $\Delta T = T_f - T_i$, then the heat, q, required to heat the system by ΔT is:

$$q = C_p \, \Delta T \tag{1}$$

where C_p is the isobaric heat capacity of the *whole* system.

This heat comes from the enthalpy change of the reaction:

$$q = -\Delta_r H$$

(*Note:* remember the reaction is exothermic *i.e.* ΔH is *negative*)

We therefore have:

$$-\Delta_r H = C_p \, \Delta T \tag{2}$$

We use a reaction of known $\Delta_r H$ to calibrate the calorimeter (*i.e.* determine C_p). We use the equation:

$$C_p = -\Delta_r H \, / \, \Delta T \tag{3}$$

N.B. In this experiment, $\Delta_r H$ is *negative* because the reaction is exothermic, and so C_p is positive.

The calorimeter is then used to measure the molar enthalpy change for the unknown reaction, we reapply the equation:

$$-\Delta_r H = C_p \, \Delta T \tag{2}$$

where ΔT is the rise in temperature for the unknown reaction.

EXPERIMENTAL PROCEDURE

Equipment:

Isobaric calorimeter with stirrer and precision thermometer

100 mL volumetric flask

250 mL measuring cylinder

10 mL pipette

Chronometer

Pipette filler

Wash bottle

Spatula
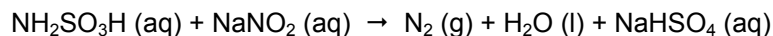
Weighing boats

Chemicals:

Sodium nitrite $NaNO_2$

Sulphamic acid NH_2SO_3H

100 volume hydrogen peroxide solution H_2O_2

Manganese dioxide MnO_2

Calibration: Measurement of the Heat Capacity of the Calorimeter

The reaction between sulphamic acid and sodium nitrite in aqueous solution is used:

$$NH_2SO_3H \text{ (aq)} + NaNO_2 \text{ (aq)} \rightarrow N_2 \text{ (g)} + H_2O \text{ (l)} + NaHSO_4 \text{ (aq)}$$

For this reaction at 25 °C, $\Delta_r H_m = -420.5 \text{ kJ mol}^{-1}$.

- Accurately weigh out 11.30 g of $NaNO_2$, dissolve in distilled water and make up to 100 mL in a 100 mL volumetric flask. Mix thoroughly.

- Transfer 600 mL of distilled water to the calorimeter, add approximately 5 g of sulphamic acid, and put the lid on. Attach the stirrer cable.

- Switch on the stirrer and allow ten minutes for the sulphamic acid to dissolve completely and for an equilibrium rate of temperature rise to be established.

- Start the chronometer and take temperature readings at one minute intervals for five minutes to define the slope of the pre-reaction period.

- On five minutes, pipette 10 mL of the $NaNO_2$ solution into the calorimeter through the open glass tube in the lid. The temperature rises rapidly. By six minutes the actual reaction should be complete. Continue taking readings at one minute intervals from six minutes to ten minutes to establish the slope of the post-reaction period.

- Empty, clean and dry the calorimeter.

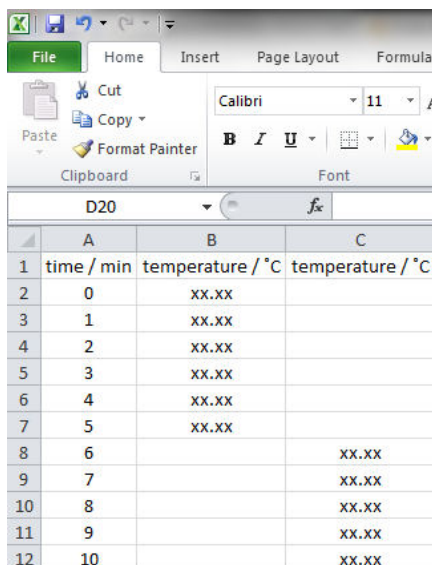## Measurement of the Enthalpy of Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide is:

$$H_2O_2 \text{ (aq)} \rightarrow H_2O \text{ (l)} + \tfrac{1}{2} O_2 \text{ (g)}$$
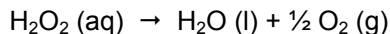
- Transfer 600 mL of distilled water to the calorimeter and put the lid on. Attach the stirrer cable. Pipette 10 mL of the hydrogen peroxide solution into the calorimeter.

- Switch on the stirrer and allow ten minutes for an equilibrium rate of temperature rise to be established.

- Weigh out roughly 6 g of manganese dioxide.

- Start the chronometer and take temperature readings at one minute intervals for five minutes to define the slope of the pre-reaction period.

- On five minutes, add the manganese dioxide through the open glass tube in the lid to catalyse the decomposition. The temperature rises rapidly. By six minutes the actual reaction should be complete. Continue taking readings at one minute intervals from six minutes to ten minutes to establish the slope of the post-reaction period.

- Empty, clean and dry the calorimeter.

DATA TREATMENT

For each reaction in turn type your values into Microsoft Excel, or any other suitable spreadsheet package or draw your own table. Put your times from 0 to 10 minutes in the first column, your pre-reaction temperatures in the second column and your post-reaction temperatures in the third column as shown in figure 2.

Figure 2: Schematic data layout.

Drag a box around the complete set of data and insert or draw a scatter graph (do not connect the points). Add a linear trendline to each of the two data sets, for the pre-reaction temperatures forecast the line forwards and for the post-reaction temperatures forecast the line backwards. Draw a vertical line at five and a half minutes and where this line intersects your extrapolations will give you T_i and T_f. Your graph should resemble figure 1. ΔT is simply then $T_f - T_i$.

Calorimeter calibration

(i)   The sulphamic acid was used in excess, hence the number of moles of reaction is equal to the number of moles of $NaNO_2$ reacting. Calculate the quantity of $NaNO_2$ added to the calorimeter in moles.

(ii)   Given that $\Delta_r H_m$ for the calibration reaction is -420.5 kJ mol^{-1}, calculate $\Delta_r H$ using your quantity of sodium nitrate and hence determine C_p using equation [3]. Hint: bear in mind the units, 1 kJ = 1000 J.
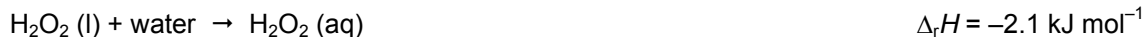
Enthalpy of decomposition of H_2O_2

(i)   The calorimeter contains the same volume of solution in both calibration and decomposition experiments so we can assume the same heat capacity. From the observed temperature rise and C_p, calculate $\Delta_r H$ for the H_2O_2 decomposed in the calorimeter using equation [2].

(ii)   The hydrogen peroxide used was 100 volume, meaning it releases 100 times its own volume of oxygen gas upon decomposition. Its concentration was determined, by titration against standard potassium permanganate solution, as 8.920 mol dm^{-3}. Given this concentration, calculate the quantity of H_2O_2 added to the calorimeter in moles.

(iii) From the number of moles of H_2O_2 added to the calorimeter, calculate $\Delta_r H_m$, in units of kJ mol^{-1}, for the decomposition.

(iv)   The experiment measures the enthalpy of decomposition of H_2O_2 in aqueous solution, *i.e.* Δ_rH for the reaction:

H_2O_2 (aq) $\rightarrow$ H_2O (l) + ½ O_2 (g)
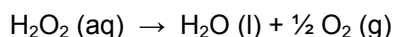
For the dissolution of pure liquid H_2O_2 in a large excess of water:

H_2O_2 (l) + water $\rightarrow$ H_2O_2 (aq) $\Delta_rH = -2.1$ kJ mol^{-1}

Use Hess' Law to calculate the enthalpy for the decomposition of liquid H_2O_2.

H_2O_2 (l) $\rightarrow$ H_2O (l) + ½ O_2 (g)
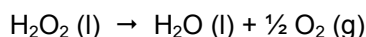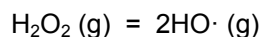
Calculation of the O–O bond dissociation energy in H_2O_2

(i)   Write out the equation for the decomposition of pure H_2O_2 (l). Above the arrow, write in the value you obtained for the reaction enthalpy in the previous part. Leave a little space and then underneath the equation write elements in their standard states. Draw an arrow from there up to each substance. The arrows represent the enthalpies of formation of the species. Bearing in mind the enthalpy of formation of O_2 (g) is zero and given the enthalpy of formation of liquid water is -285.8 kJ mol^{-1} it is now possible to determine the enthalpy of formation of liquid hydrogen peroxide using a Hess' Law cycle.

(ii)   The enthalpy of vaporisation of H_2O_2, $\Delta_{vap}H$, is Δ_rH for the process:

H_2O_2 (l) $\rightarrow$ H_2O_2 (g)
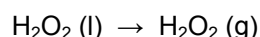
Given the value of $\Delta_{vap}H$ is $+48.5$ kJ mol^{-1}, once again write elements in their standard states under this equation, draw arrows and using Hess' Law calculate the enthalpy of formation of gaseous hydrogen peroxide.

(iii) The dissociation energy of the (O–O) bond in hydrogen peroxide, written D(HO–OH), is Δ_rH for the process

$$H_2O_2 \text{ (g) } = \text{ 2HO· (g)}$$

Given the value of Δ_fH for OH· (g) is $+33.9$ kJ mol^{-1}, once more, write elements in the standard states under this equation, draw arrows and using Hess' Law calculate D(HO–OH)

Finally, the dissociation energy of the O–O bond in the oxygen molecule, $D(O_2)$, is 498.3 kJ mol^{-1}. This should be significantly higher than the value you have just calculated for the dissociation energy of the O–O bond in H_2O_2, D(HO–OH). Whilst there is no extra credit for doing so, can you think of a reason why this might be?

You will be assessed on your calculated values for the enthalpy of decomposition of liquid hydrogen peroxide and, D(HO–OH), the bond dissociation energy of hydrogen peroxide.