Thermodynamics Experiment

The Enthalpy of H_2O_2 Decomposition in Aqueous Solution

INTRODUCTION

The aim of this experiment is to illustrate the use of calorimetry in the measurement of thermodynamic data and to illustrate the use of basic thermodynamics to calculate enthalpies of reaction and bond dissociation energies.
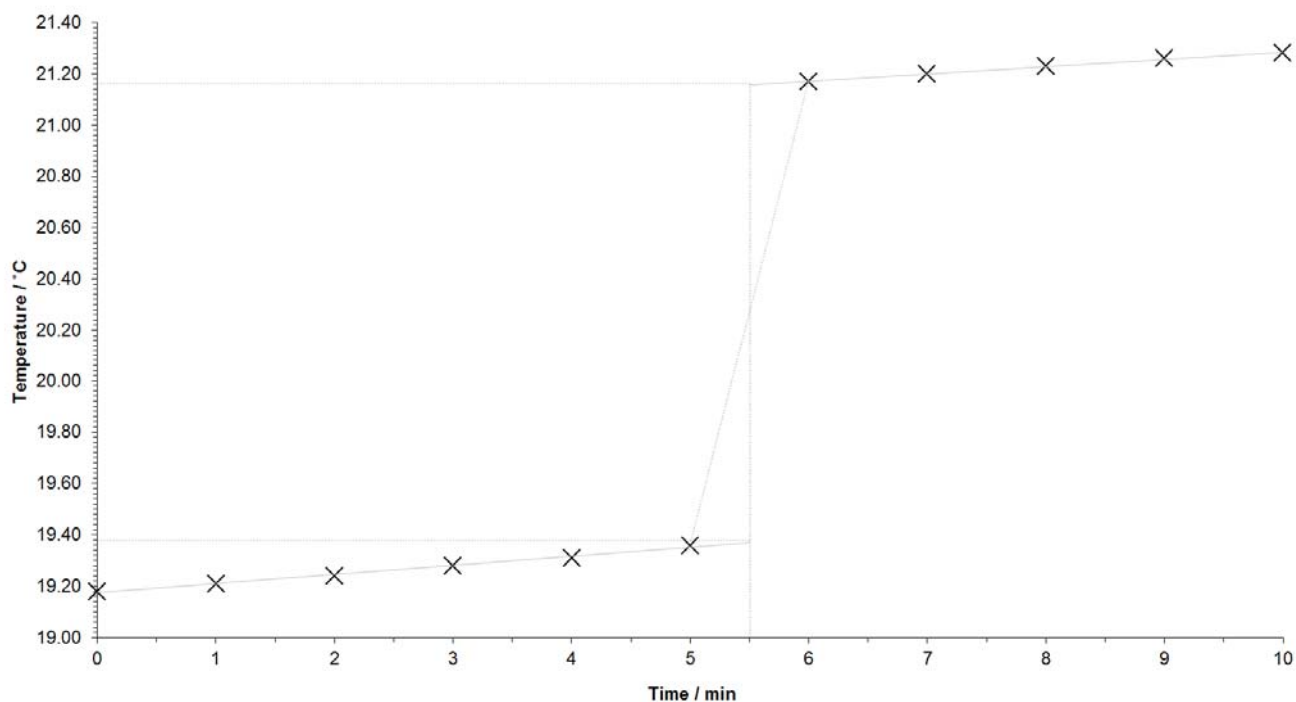
RESULTS

The mass of sodium nitrate $NaNO_2$ = 11.30 g.

The mass of sulphamic acid NH_2SO_3H = 5.00 g.

The mass of manganese dioxide MnO_2 = 6.00 g.

The concentration of hydrogen peroxide = 8.920 mol dm^{-3}.

Calibration of the calorimeter		Decomposition of Hydrogen Peroxide	
time / min	temperature / ˚C	time / min	temperature / ˚C
0	19.18	0	19.43
1	19.21	1	19.45
2	19.24	2	19.47
3	19.28	3	19.50
4	19.31	4	19.52
5	19.36	5	19.54
6	21.17	6	21.67
7	21.20	7	21.70
8	21.23	8	21.74
9	21.26	9	21.78
10	21.28	10	21.82

DATA TREATMENT

Temperature rise = 21.16 – 19.38 ˚C = 1.78 ˚C or 1.78 K
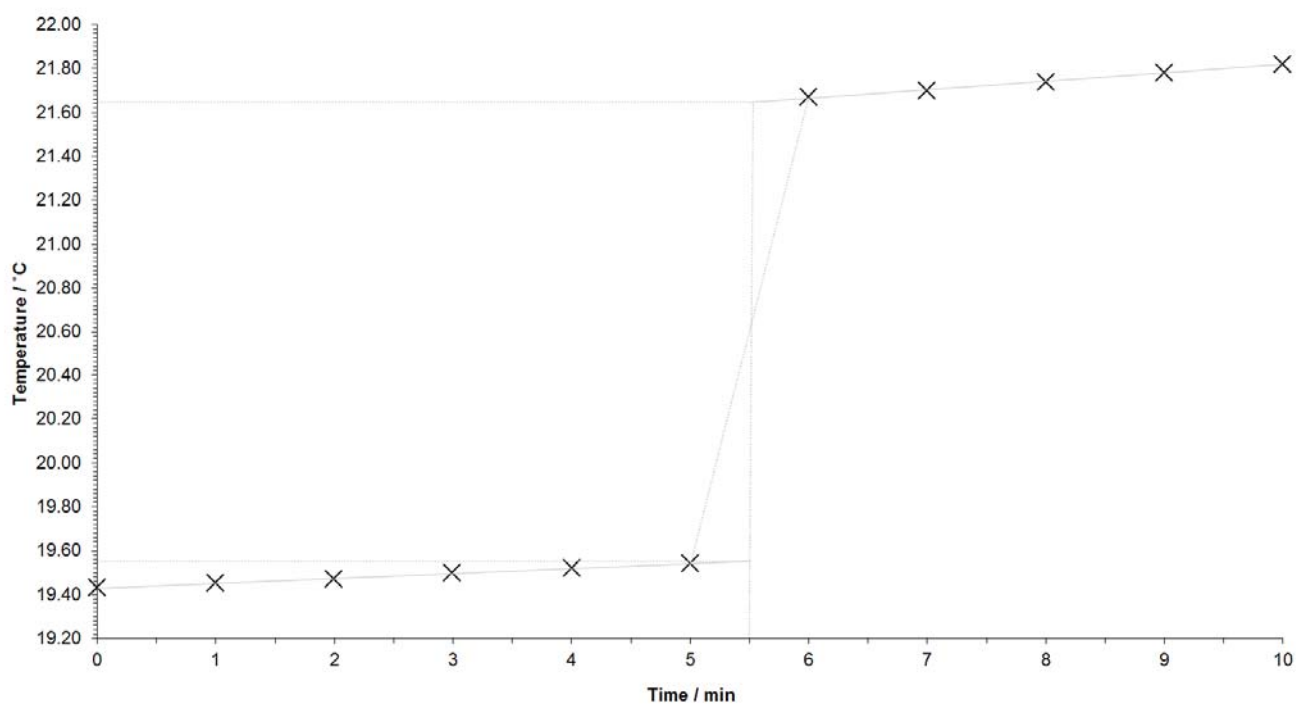
Temperature rise = 21.65 – 19.55 ˚C = 2.10 ˚C or 2.10 K

Calorimeter Calibration

(i) The amount of $NaNO_2$ = 11.30 g / 68.9953 g mol^{-1} = 0.1638 mol

However this was dissolved in 100 cm^3 and then only 10 cm^3 of the resulting solution were pipetted into the calorimeter so the amount of $NaNO_2$ used in the calibration is 0.01683 mol. Since the sulphamic acid is in excess this governs the amount of reaction.

(ii) Given that Δ_rH_m for the calibration reaction is –420.5 kJ mol^{-1} the isobaric heat capacity of the calorimeter, C_p, may be calculated as follows:

C_p = q_p / ΔT = $-\Delta H$ / ΔT = –(–420.5 kJ mol^{-1}) × 0.01683 mol / 1.78 K = 3.976 kJ K^{-1} or 3976 J K^{-1}

Enthalpy of Decomposition of H_2O_2

(i) The H_2O_2 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}.

Moles of H_2O_2 decomposed in the calorimeter =

$8.920 \, \text{mol dm}^{-3} \times \dfrac{10 \, \text{cm}^3}{1000 \, \text{cm}^3 \, \text{dm}^{-3}} = 0.0892 \, \text{mol}$. Since the manganese dioxide was in excess this governs the amount of reaction.

(ii) The enthalpy change $\Delta H = -C_p \Delta T$ = –3976 J K^{-1} × 2.10 K = –8350 J or 8.35 kJ

(iii) Δ_rH_m = –8.35 kJ / 0.0892 mol = –93.6 kJ mol^{-1}.

(iv) We have now determined Δ_rH_m = –93.6 kJ mol^{-1} for the reaction:

H_2O_2 (aq) $\rightarrow$ H_2O (l) + ½O_2 (g)

Given that Δ_rH_m = –2.1 kJ mol^{-1} for the reaction:

H_2O_2 (l) $\rightarrow$ H_2O_2 (aq)

We now need to determine Δ_rH_m for the reaction:

H_2O_2 (l) $\rightarrow$ H_2O (l) + ½O_2 (g)

Using Hess' Law Δ_rH_m = –93.6 kJ mol^{-1} –2.1 kJ mol^{-1} = –95.7 kJ mol^{-1}

The enthalpy of decomposition of H_2O_2 (l) is thus –95.7 kJ mol^{-1}.

Calculation of the O-O bond dissociation energy in H_2O_2

(i)
$$\begin{array}{ccc} & -95.7 & \\ H_2O_2 \text{ (l)} & \rightarrow & H_2O \text{ (l)} + \text{½}O_2 \text{ (g)} \end{array}$$

$\Delta_fH(H_2O_{2\text{ (l)}})\uparrow$ $-285.8\uparrow$ $0\uparrow$

elements in their standard states   [values quoted in kJ mol^{-1}]

$\Delta_fH(H_2O_{2\text{ (l)}})$ = –258.8 kJ mol^{-1} –(–95.7 kJ mol^{-1}) = –190.1 kJ mol^{-1}

(ii)   +48.5
$$H_2O_2 \text{ (l)} \quad \rightarrow \quad H_2O_2 \text{ (g)}$$

−190.1 ↑ $\Delta_f H(H_2O_2 \text{ (g)})$ ↑

        elements in their standard states   [values quoted in kJ mol^{-1}]

$\Delta_f H(H_2O_2 \text{ (g)})$ = −190.1 kJ mol^{-1} + 48.5 kJ mol^{-1} = −141.6.1 kJ mol^{-1}

(iii) D(HO–OH) = 2 × (+33.9 kJ mol^{-1}) − (−141.6 kJ mol^{-1}) = 209.4 kJ mol^{-1}

(iv) $D(O_2)$ = 498.3 kJ mol^{-1}. The discrepancy lies in the difference in the two bonds. In oxygen the bond is a double bond whereas in hydrogen peroxide the bond is a single bond.

CONCLUSIONS

Hopefully this virtual practical has served to highlight the technique of calorimetry and the application of basic thermodynamics. The method works well, evidenced by the good agreement between experimental and literature values.

Enthalpy of formation of liquid hydrogen peroxide: −190.1 kJ mol^{-1} compared to −187.6 kJ mol^{-1} error = 1.3%

[CRC Handbook of Chemistry and Physics]

O–O bond dissociation energy of hydrogen peroxide: +209.4 kJ mol^{-1} compared to +213.4 kJ mol^{-1} error = 1.9%

[Cottrell 'Strengths of Chemical Bonds'].