Marks 4

- A solution of 2.00 M NaOH (50.0 mL) at 44.9 ºC is added to a constant pressure ("coffee cup") calorimeter containing 250.0 mL of 0.70 M HNO_3 at 21.5 ºC. The final temperature of the solution is 29.9 ºC. Calculate the enthalpy of neutralisation of OH^-(aq) and H^+(aq) in kJ mol^{-1}. Assume the density of these solutions is 1.000 g mL^{-1} and the specific heat capacity of the solutions is 4.184 J K^{-1} g^{-1}.

The final temperature is due to both the mixing of two solutions with different initial temperatures and the chemical reaction. It is convenient to treat these two processes separately.

(i) Temperature change due to mixing:

The NaOH(aq) and HNO_3(aq) solutions are initially at 44.9 °C and 21.5 °C. When mixed, heat from the former will warm up the latter to give a solution with temperature T_m.

50.0 mL of NaOH(aq) corresponds to (50.0 mL × 1.000 g mL^{-1}) = 50.0 g. The heat *lost* by this mass is given by:

$$q_1 = mC\Delta T = 50.0 \times 4.184 \times (T_m - 44.9)$$

250.0 mL of HNO_3(aq) corresponds to (250.0 mL × 1.000 g mL^{-1}) = 250.0 g. The heat *gained* by this mass is given by:

$$q_2 = mC\Delta T = 250.0 \times 4.184 \times (T_m - 21.5)$$

As the heat lost by NaOH(aq) is gained by the HNO_3(aq), $q_1 = -q_2$ and so:

$$50.0 \times 4.184 \times (T_m - 44.9) = -1 \times 250.0 \times 4.184 \times (T_m - 21.5)$$

so T_m = 25.4 °C

(ii) Temperature change due to reaction:

The final temperature is 29.9 °C so the temperature change due to the reaction must be (29.9 – T_m) = (29.9 – 25.4) = 4.5 °C. The mixed solution has a total volume of (50.0 + 250.0) = 300.0 mL.

This volume has a mass of (300.0 mL × 1.000 g mL^{-1}) = 300.0 g. The heat change corresponding to this mass and temperature increase is therefore:

$$q_r = mC\Delta T = 300.0 \times 4.184 \times 4.5 = 5600 \text{ J} = 5.6 \text{ kJ}$$

The reaction is a 1:1 neutralization reaction, $OH^-(aq) + H^+(aq) \rightarrow H_2O(aq)$.

ANSWER CONTINUES ON THE NEXT PAGE

The number of moles of OH^-(aq) present in 50.0 mL of the 2.00 M NaOH solution is:

number of moles = concentration × volume = 2.00 × 0.0500 = 0.100 mol

The number of moles of H^+(aq) present in 250.0 mL of the 0.70 M HNO_3 solution is:

number of moles = concentration × volume = 0.70 × 0.2500 = 0.175 mol

The H^+ is therefore in excess and the OH^- is the limiting reagent.

As 0.100 mol generates a heat change of 5.6 J, the enthalpy of neutralization is:

$$\Delta_r H = \frac{-5.6\,\text{kJ}}{0.1\,\text{mol}} = -56\ \text{kJ}\,\text{mol}^{-1}$$

The reaction increases the temperature and so must be exothermic.

Answer: **56 kJ mol^{-1}**

Calculate the pH in the combined solution in the calorimeter at 21.5 ºC.

As 0.100 mol of OH^-(aq) reacts with 0.175 mol of H^+(aq), the final solution contains (0.175 – 0.100) = 0.075 mol of unreacted H^+(aq).

The final solution has a volume of 300.0 mL so,

$$[H^+(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.075\,\text{mol}}{0.3000\,\text{L}} = 0.25\,\text{M}$$

Hence,

$$pH = -\log_{10}[H^+(aq)] = -\log_{10}(0.25) = 0.60$$

Answer: **pH = 0.60**