**Marks
6**

- High-purity benzoic acid, C_6H_5COOH, ($\Delta H°_{comb} = -3227$ kJ mol^{-1}) is used to calibrate a bomb calorimeter that has a 1.000 L capacity. A 1.000 g sample of C_6H_5COOH is placed in the bomb calorimeter, along with 750 mL of pure $H_2O(l)$, and the remaining 250 mL cavity is filled with pure $O_2(g)$ at 10.00 atm. The C_6H_5COOH is ignited and completely burned, causing the temperature of the water and the bomb calorimeter to rise from 27.20 °C to 33.16 °C. Write the chemical equation corresponding to the standard enthalpy of combustion ($\Delta H°_{comb}$) of C_6H_5COOH.

$$C_6H_5COOH(s) + \frac{15}{2} O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l)$$
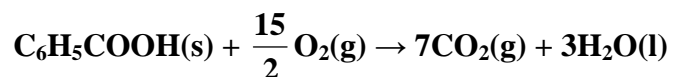
Given that $H_2O(l)$ has a heat capacity of 4.184 J K^{-1} g^{-1} and a density of 0.997 g mL^{-1}, calculate the heat capacity of the bomb calorimeter itself (in units of J K^{-1}). Ignore the heat capacity of the gases and of C_6H_5COOH.

The molar mass of C_6H_5COOH is (7×12.01 (C))+(6×1.008 (H))+(2×16.00 (O)) = 122.118. Therefore 1.000 g corresponds to:

$$\text{amount of } C_6H_5COOH = \frac{\text{mass}}{\text{molar mass}} = \frac{1.000}{122.118} = 0.008189 \text{ mol}$$

As combustion of 1 mol gives out 3227 kJ of heat, this amount gives out:

$$q = 0.008189 \times 3227 = 26.42 \text{ kJ} = 26.43 \times 10^3 \text{ J}$$

This heat leads to a temperature increase of (33.16 – 27.20) = 5.96 °C for the combination of the calorimeter and the water. As water has a density of 0.997 g mL^{-1}, 750 mL has a mass of 750 × 0.997 g.

$$q = (mC_{water} + C_{calorimeter}) \times \Delta T$$
$$= ((750 \times 0.997 \times 4.184) + (C_{calorimeter})) \times 5.96 = 26.42 \times 10^3$$

$$C_{calorimeter} = 1305 \text{ J K}^{-1}$$

Answer: **1305 J K^{-1}**

ANSWER CONTINUES ON THE NEXT PAGE

If 30.0% of the CO_2 produced dissolves in the water, calculate the final total pressure (in atm) inside the 250 mL cavity of the bomb calorimeter. Assume oxygen is insoluble in water and ignore the vapour pressure of water.

Initially, 10.00 atm of oxygen is present in a volume of 250 mL and a temperature of 27.20 °C. Using the ideal gas equation, PV = nRT,

$$\text{initial } n_{O_2(g)} = \frac{PV}{RT} = \frac{(10.00) \times (0.250)}{(0.08206) \times (273 + 27.20)} = 0.1015 \text{ mol}$$

From the chemical equation, $\dfrac{15}{2}$ mol of O_2 are required for the combustion of every mole of C_6H_5COOH. As 0.008189 mol of C_6H_5COOH is present,

$$\text{consumed } n_{O_2(g)} = 0.008189 \times \frac{15}{2} = 0.06142 \text{ mol}$$

Therefore,

$$\text{final } n_{O_2(g)} = 0.1015 - 0.06142 = 0.0400 \text{ mol}$$

From the chemical equation, 7 moles of CO_2 are produced for the combustion every mole of C_6H_5COOH. As 0.008189 mol of C_6H_5COOH is present,

$$\text{total } n_{CO_2} = 0.008189 \times 7 = 0.05732 \text{ mol}$$

As 30% of this dissolves,

$$n_{CO_2(g)} = 0.70 \times 0.05732 = 0.04013 \text{ mol}$$

The total number of moles of $O_2(g)$ and $CO_2(g)$ is therefore 0.0400 + 0.04013 = 0.0801. This is present in 250 mL at 33.16 °C. Using the ideal gas law,

$$P = \frac{nRT}{V} = \frac{(0.0801) \times (0.08206) \times (273 + 33.16)}{0.250} = 8.05 \text{ atm}$$

Answer: **8.05 atm**