Question 39 **(12 marks)**

Fluorescent lights are glass tubes which are coated on the inside with rare earth metal phosphates (such as cerium, lanthanum and terbium phosphates) that provide light. Cerium, lanthanum and terbium are expensive, so are recovered once the fluorescent light is no longer functional.

The key steps in one method proposed for recovery of these rare earth metals are summarised below:

- **Step 1:** Physical separation of the rare earth metal phosphates from the glass and any metallic components. This gives an impure powder consisting of cerium, lanthanum and terbium phosphates.
- **Step 2:** Add excess solid sodium carbonate to the powder and heat, completely converting each rare earth metal phosphate to its corresponding oxide, as shown by the following balanced equations:

  $2\ LaPO_4(s) + 3\ Na_2CO_3(s) \rightarrow La_2O_3(s) + 2\ Na_3PO_4(s) + 3\ CO_2(g)$

  $4\ CePO_4(s) + 6\ Na_2CO_3(s) + O_2(g) \rightarrow 4\ CeO_2(s) + 4\ Na_3PO_4(s) + 6\ CO_2(g)$

  $2\ TbPO_4(s) + 3\ Na_2CO_3(s) \rightarrow Tb_2O_3(s) + 2\ Na_3PO_4(s) + 3\ CO_2(g)$
- **Step 3:** Wash the product from Step 2 with water.
- **Step 4:** Add hydrochloric acid to the washed product from Step 3 to leach (dissolve) only the rare earth metal oxides.
- **Step 5:** Use solvent extraction to separate the different rare earth metals from each other and create separate solutions of each of them.
- **Step 6:** Add oxalic acid to the separated solutions to precipitate the rare earth metal ions as oxalate salts.
- **Step 7:** Heat the oxalate salts to recover the rare earth metals as pure oxides, namely La_2O_3, Tb_4O_7 and CeO_2.

A chemist used the above procedure to determine the percentage by mass of lanthanum, terbium and cerium in some fluorescent lights and, after completing Step 1, had recovered 1.20 kg of the coating chemicals.

(a) At the completion of Step 2, the mass of the mixture had decreased by 11.3 g. Calculate the mass of sodium carbonate that reacted with the rare earth metal phosphates.

(3 marks)

The mass of the solid sent from Step 3 to Step 4 was 1.16 kg. This solid was leached with 6.00 mol L^{-1} HCℓ at a solid to liquid ratio of 150 g per litre. Analysis of the solution at the end of leaching showed that it contained lanthanum, terbium and cerium, with its lanthanum concentration being 8.65×10^{-3} mol L^{-1}.

(b) Calculate the percentage, by mass, of lanthanum in the fluorescent light coating chemical, given that the leaching efficiency for lanthanum was 86%.

Note that the balanced equation for the leaching of lanthanum with hydrochloric acid is:

$$La_2O_3(s) + 6\ HC\ell(aq) \rightarrow 2\ LaC\ell_3(aq) + 3\ H_2O(\ell)$$

(5 marks)

Analysis of the cerium-containing solution produced in Step 5 showed that its cerium concentration was 0.146 mol L^{-1}. This solution, which had a volume of 424 mL, was added to 110 mL of aqueous 1.15 mol L^{-1} oxalic acid during Step 6, resulting in the precipitation of cerium oxalate, $Ce(C_2O_4)_2$. The balanced equation for this reaction is:

$$CeC\ell_4(aq) + 2\ H_2C_2O_4(aq) \rightarrow Ce(C_2O_4)_2(s) + 4\ HC\ell(aq)$$

(c) Did the chemist add enough oxalic acid solution to precipitate all of the cerium? Use calculations to support your answer. (4 marks)