Chemguide – answers

PHENYLAMINE: PREPARATION

1. a) React with concentrated nitric acid and concentrated sulphuric acid at a temperature not exceeding 50°C for about half-an-hour.

b) At a higher temperature you can get more than one NO₂ group substituted into the ring.

c) $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$

(You can draw the benzene rings if you want to. For an equation like this, it doesn't really matter which form you use.)

d) In the first step, you heat the nitrobenzene under reflux with tin and concentrated hydrochloric acid for about half-an-hour. In the second step, you add sodium hydroxide solution to the reaction mixture.

e) The reduction of the nitrobenzene takes place under strongly acidic conditions, and so you get the salt of phenylamine formed instead of free phenylamine. The sodium hydroxide solution releases the free amine from the salt.

f) $C_6H_5NO_2 + 7H^+ + 6e^- - C_6H_5NH_3^+ + 2H_2O$

Problems working this out? Do NOT try to learn it – you need to be able to work out equations like this wherever they come up.

Start with what you know:

 $C_6H_5NO_2 \longrightarrow C_6H_5NH_3^+$

All you can add to this for a reaction under acidic conditions is water, hydrogen ions and electrons.

The oxygen on the left-hand side must end up as water:

 $C_6H_5NO_2 \longrightarrow C_6H_5NH_3^+ + 2H_2O$

The extra hydrogens on the right-hand side must come from hydrogen ions:

$$C_6H_5NO_2 + 7H^+ \longrightarrow C_6H_5NH_3^+ + 2H_2O$$

Finally balance the charges by adding electrons:

 $C_{6}H_{5}NO_{2} + 7H^{+} + 6e^{-} \rightarrow C_{6}H_{5}NH_{3}^{+} + 2H_{2}O$

(I know I said on the Chemguide page that you probably won't need to have to do this in this context, but it is something you will have to do elsewhere in your course. The more you practise the better!)

g) $C_6H_5NH_3^+ + OH^- \longrightarrow C_6H_5NH_2 + H_2O$