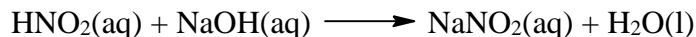


Solution to:

HNO₂ is a weak acid with a K_a = 1.9 x 10⁻⁴. A 20.00 mL aliquot of a 2.000 M solution of HNO₂ was titrated with 2.000 M NaOH. The indicator used had a pK_{ind} = 4.50.

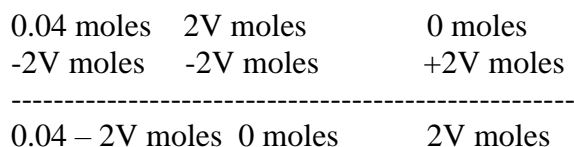
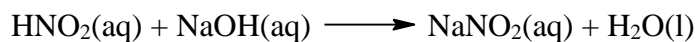
a) At what volume of added NaOH will the end point of the titration be reached?

First off, looking at the pK_{ind}, we see that the end point will be reached while the solution is still acidic. This therefore means that for the reaction



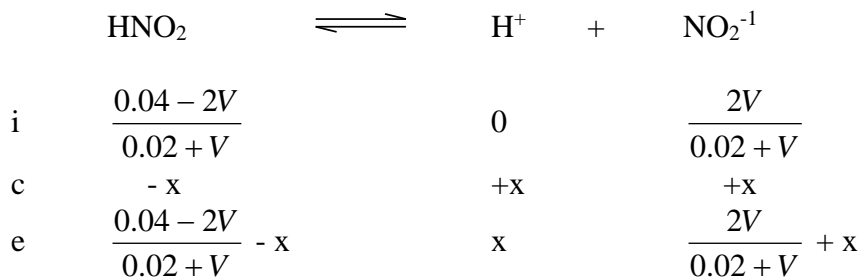
the acid is in excess.

With that out of the way, we go through the usual routine. That is, we'll let the volume of added NaOH at the end point be "V" L. This means, then, that for the reaction between acid and base, we have:



The concentration of excess acid is therefore $\frac{0.04 - 2V}{0.02 + V}$ moles per litre, and the salt is $\frac{2V}{0.02 + V}$ moles per litre.

These concentrations go into the equilibrium chart in the usual way:



We know that the solution will change colour at pH = 4.50, so that means the [H⁺] = 10^{-4.50} = 3.2 x 10⁻⁵. From the chart above, this is the value of x.

Also: The equilibrium expression is:

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

Putting in the expressions for the various concentrations, as well as the value of x that we found, gives:

$$1.9 \times 10^{-4} = 3.2 \times 10^{-5} \left(\frac{\left(\frac{2V}{0.02 + V} + 3.2 \times 10^{-5} \right)}{\left(\frac{0.04 - 2V}{0.02 + V} - 3.2 \times 10^{-5} \right)} \right)$$

This expression looks rather complex. We can, however, make an assumption that will simplify it dramatically. Specifically, if we assume that the $[H^+]$ is small compared to the concentrations of the NO_2^- anion and the HNO_2 , then the expression becomes:

$$1.9 \times 10^{-4} = 3.2 \times 10^{-5} \left(\frac{\left(\frac{2V}{0.02 + V} \right)}{\left(\frac{0.04 - 2V}{0.02 + V} \right)} \right)$$

The total volumes cancel top and bottom, and the expression simplifies still further:

$$1.9 \times 10^{-4} = 3.2 \times 10^{-5} \left(\frac{(2V)}{(0.04 - 2V)} \right)$$

This is rather easier to work with. Solving for V gives 0.01715 L, or 17.15 mL. (Incidentally, solving the full expression gives the same answer to the nearest 0.01 mL.)

So: The end point will be reached at 17.15 mL of added base.

b) Is this a good indicator to use for this titration?

To answer that, we need to know how much base we need to reach the equivalence point. To figure that out:

$$0.02000L \times \frac{2.000 \text{ moles } HNO_2}{L} \times \frac{1 \text{ NaOH}}{1 HNO_2} \times \frac{1 \text{ litre}}{2.000 \text{ moles NaOH}} \times \frac{1000 \text{ mL}}{1 L} = 20.00 \text{ mL}$$

So we need 20.00 mL to reach the equivalence point, but the indicator changes colour at 17.15 mL, or 2.85 mL too early. This represents a 14.25 percent error, which is clearly unacceptable for a titration (we need 0.5 percent or less).

Good test question, isn't it?