CHEMISTRY · YEAR 12 · PRACTICAL 4

4 Acid–base titration: how acidic is vinegar?

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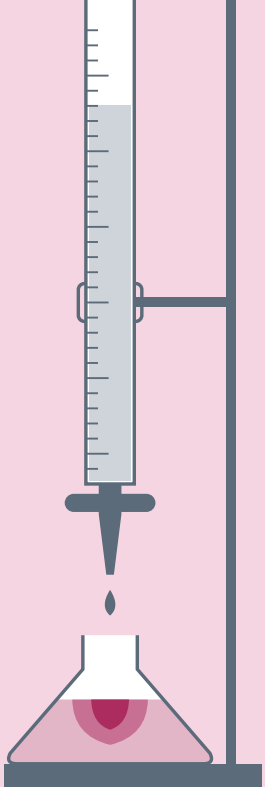

ABSTRACT

We titrated a cider vinegar with 0.100 mol·dm^{-3} sodium hydroxide and phenolphthalein to measure its acetic acid. Three concordant titrations used a mean of 20.87 cm^3 of NaOH: the vinegar holds 0.835 mol·dm^{-3} of CH_3COOH, or 5.01 ± 0.04 g in every 100 cm^3, in agreement with the 5 % stated on the label. Another titration, followed with a pH meter, gave the titration curve and a pK_a of 4.75.

1 Aim

To find how much acetic acid (CH_3COOH) a shop-bought vinegar holds by titration with a strong base, and to check the acidity on its label; then to record the pH curve and estimate from it the acid dissociation constant.

2 Background

Vinegar is a dilute aqueous solution of acetic acid, a weak acid, and the OH^- ions of sodium hydroxide neutralise it mole for mole:

$$CH_3COOH\,(aq) + NaOH\,(aq) \longrightarrow CH_3COONa\,(aq) + H_2O\,(l)$$

At the equivalence point as much base has been added as there was acid, and since the amount of substance is $n = cV$, the acid's concentration follows from the volume of base used. Solid NaOH takes up water and CO_2 from the air, so weighing it cannot fix the concentration: the solution was standardised the day before against a primary standard, potassium hydrogen phthalate ($KHC_8H_4O_4$).

At equivalence the flask holds neither acid nor base, only sodium acetate, and the acetate ion, CH_3COO^-, is a weak base: $K_b = K_w/K_a = 5.7 \times 10^{-10}$. At that point its concentration c is about 0.045 mol·dm^{-3}, so

$$[OH^-] = \sqrt{K_b\,c} = 5.1 \times 10^{-6}\ \text{mol·dm}^{-3}, \qquad \text{pH} = 14 - \text{pOH} = 8.7$$

The pH at equivalence is therefore not 7, and that is why the indicator is phenolphthalein, colourless below pH 8.2 and pink above it, which changes colour inside the steep rise in pH around equivalence. Before the rise, the Henderson–Hasselbalch equation gives the pH of the buffer that the acid and acetate form:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

With half the base added, the two concentrations are equal and the pH equals the $\mathrm{p}K_\mathrm{a}$ of the acid, which the literature gives as 4.76 at 25 °C.

3 Apparatus and chemicals

- A 50 cm³ burette (±0.05 cm³), 10 and 25 cm³ bulb pipettes and a pipette filler, a 100 cm³ volumetric flask and three 250 cm³ conical flasks.
- A pH meter calibrated with pH 4.00 and 7.00 buffers, a magnetic stirrer and a white tile.
- Sodium hydroxide solution standardised at 0.100 mol·dm⁻³, and phenolphthalein, 0.5 % in ethanol.
- A small funnel for filling the burette, and a wash bottle.
- Cider vinegar with a stated acidity of 5 %, and distilled water.

> **SAFETY**
>
> NaOH solution irritates the eyes and skin even when dilute, so we wore safety glasses the whole time. We filled the pipettes with a filler, never by mouth, and the burette below eye level, through a funnel that we took out before reading it. The phenolphthalein is dissolved in ethanol, which is flammable, so there were no flames on the bench. A splash on the skin was rinsed off at once with plenty of water.

4 Method

1. We pipetted 10 cm³ of vinegar into the 100 cm³ volumetric flask, made it up to the mark with distilled water and inverted it a few times to mix: a tenfold dilution.
2. We rinsed the burette with a little of the NaOH solution, filled it, cleared the bubble from the tip and recorded the initial reading, with our eyes level with the meniscus.
3. We pipetted 25.0 cm³ of the diluted vinegar into a conical flask, stood it on the white tile and added three drops of phenolphthalein.
4. We added the NaOH while swirling the flask. When the pink began to take longer to fade, we went on drop by drop until a pale pink lasted half a minute, and recorded the final reading.
5. We carried out a rough titration, then repeated the titration until three titres were within 0.10 cm³ of each other.
6. For the curve we titrated another aliquot with the pH electrode in the flask. We added the NaOH 2 cm³ at a time, and 0.5 cm³ at a time from 18 to 24 cm³, and recorded the pH after each addition.

5 Results

5.1 Titrations with the indicator

Table 1 lists the burette readings. The rough titration went past the end point and is left out of the mean; the other three agree to within 0.05 cm³. Their mean, V_b = 20.87 cm³, has a standard deviation of 0.03 cm³.

Table 1. Burette readings, titrating 25.0 cm³ of diluted vinegar with 0.100 mol·dm⁻³ NaOH.

Titration	V_initial / cm³	V_final / cm³	V_b used / cm³
Rough	0.00	21.30	21.30
1	0.40	21.25	20.85
2	1.10	22.00	20.90
3	0.25	21.10	20.85
		Mean of 1–3	20.87
		Standard deviation	0.03

Synthetic readings, taken to the nearest 0.05 cm³, as a burette is read.

Since each aliquot was V_a = 25.0 cm³ of vinegar diluted ten times (f = 10), the concentration of acetic acid in the vinegar is

$$c_\mathrm{vinegar} = f\,\frac{c_\mathrm{b}\,V_\mathrm{b}}{V_\mathrm{a}} = 10 \cdot \frac{0.100 \cdot 20.87}{25.0}\ \mathrm{mol\cdot dm^{-3}} = 0.835\ \mathrm{mol\cdot dm^{-3}}$$

With the molar mass of acetic acid, 60.05 g·mol⁻¹, that is 50.1 g·dm⁻³, or 5.01 g in every 100 cm³ of vinegar. Combining the tolerances of the glassware with that of the NaOH concentration gives a relative uncertainty of 0.7 %, so the result is 5.01 ± 0.04 g of acetic acid per 100 cm³.

5.2 The pH curve

Figure 1 plots the pH against the volume of NaOH added. The pH starts at 2.9 in the diluted vinegar and climbs slowly up to about 18 cm³, because the mixture of acid and acetate buffers it, then leaps by more than five units between 20 and 22 cm³. The steepest step, between 20.5 and 21 cm³, holds the equivalence point, which the model puts at 20.87 cm³ and pH 8.7, inside the range over which phenolphthalein changes colour. The pH at half that volume, interpolated between the readings at 10 and 12 cm³, is 4.75, which we take as the pK_a.

6 Discussion

The spread of the concordant titres, 0.03 cm³, is smaller than the tolerance of the burette, so the random error is small. The most likely error is systematic: had the NaOH absorbed CO$_2$ since it was standardised, some of it would now be carbonate, and the titre to the phenolphthalein end point would come out too high. Standardising on the day, or guarding the bottle with a soda-lime tube, would prevent it.

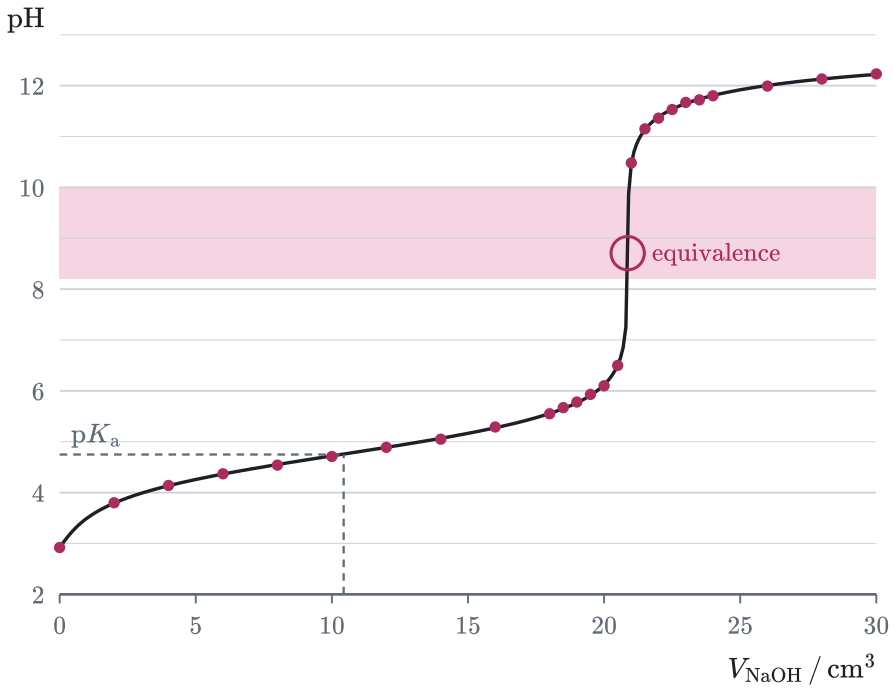

Figure 1. Titration curve of 25.0 cm³ of diluted vinegar with 0.100 mol·dm⁻³ NaOH: pH meter readings (dots) and the model with $K_a = 1.75 \times 10^{-5}$ (line). The pink band is the range over which phenolphthalein turns, pH 8.2 to 10.0.

Synthetic readings.

The curve confirms the choice of indicator: phenolphthalein first turns pink at pH 8.2, less than a drop before equivalence. Methyl orange, which changes between pH 3.1 and 4.4, would have turned before a third of the acid was neutralised. Our pK_a, 4.75, is 0.01 below the literature value.

7 Conclusion

The cider vinegar holds 0.835 mol·dm⁻³ of acetic acid, or 5.01 ± 0.04 g per 100 cm³, so the 5 % acidity on its label is right within our uncertainty. The pH curve gives acetic acid a pK_a of 4.75, which is a K_a of 1.8×10^{-5}.

References

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