

4.4.3 Drawing titration curves and resolving two neutralisation stages

Name: _____ Class: _____ Date: _____

Total: 27 marks

KEY WORDS equivalence point • diprotic acid

Objective

Draw and interpret acid–base curves, including two-stage neutralisation. Questions, models and marking guidance are original.

1 Key knowledge and worked examples

Start with reacting amounts. An equivalence point is a stoichiometric amount, not automatically pH 7. At 298 K, strong acid–strong base equivalence is near 7; weak acid–strong base is above 7; strong acid–weak base is below 7. The initial pH and excess-titrant end also depend on strength. Weak acid–weak base usually gives no sufficiently sharp vertical region for an ordinary colour indicator.

■ Worked two-stage neutralisation

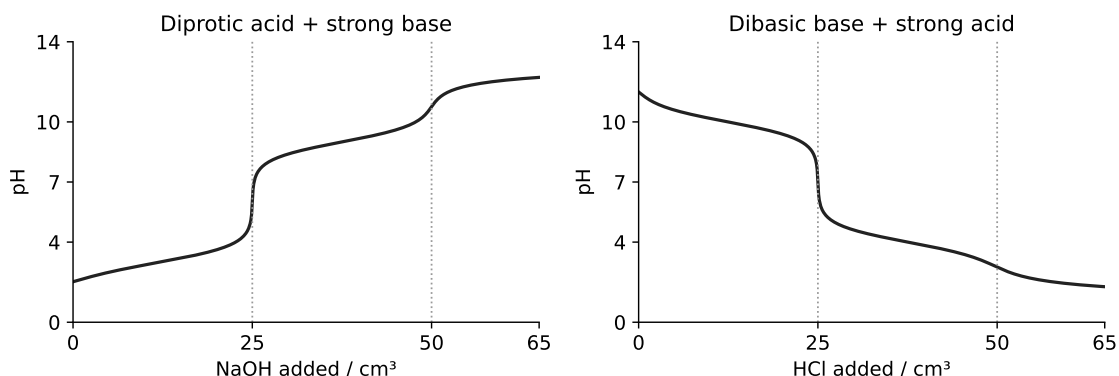
25.0 cm³ of 0.100 mol dm^{−3} H₂A contains $0.100 \times 0.0250 = 0.00250$ mol acid. With 0.100 mol dm^{−3} NaOH:

- First equivalence: $\text{H}_2\text{A} + \text{OH}^- \rightarrow \text{HA}^- + \text{H}_2\text{O}$ needs 0.00250 mol OH[−], or 25.0 cm³ titrant.
- Second equivalence: $\text{HA}^- + \text{OH}^- \rightarrow \text{A}^{2-} + \text{H}_2\text{O}$ needs another 0.00250 mol, making 50.0 cm³ total.

Halfway to the first stage, the H₂A/HA[−] buffer can give $\text{pH} \approx \text{pK}_{\text{a}1}$. Halfway between the first and second stages, the HA[−]/A^{2−} buffer can give $\text{pH} \approx \text{pK}_{\text{a}2}$ when the dissociations are sufficiently distinct. Two proton equivalents do not guarantee two sharp visible jumps; the dissociation constants and concentration determine the shape.

A base B that accepts two protons reacts in stages $\text{B} \rightarrow \text{BH}^+ \rightarrow \text{BH}_2^{2+}$ when titrated with strong acid. The pH curve falls, but the 1:1 and 2:1 titrant amounts follow the same mole accounting. Do not copy the direction of an acid-plus-base curve.

Two neutralisation stages: 25.0 cm³ of 0.100 M solute + 0.100 M titrant
 Illustrative separated dissociations, 298 K; dotted lines at 25 and 50 cm³



The dotted lines mark stoichiometric stages, including a stage that need not give a sharp enough colour endpoint. Use the actual measured curve and indicator transition data to judge a usable endpoint. The illustrated constants are chosen models, not a claim about every diprotic substance.

2 Practice

2.1 State whether equivalence pH at 298 K is near, above or below 7 for strong acid–strong base, weak acid–strong base and strong acid–weak base. Explain one of the non-neutral cases using the ion present. [4]

2.2 20.0 cm³ of 0.150 mol dm⁻³ H₂A is titrated with 0.100 mol dm⁻³ NaOH. Calculate the total titrant volume at each equivalence stage. [3]

2.3 Explain why a diprotic acid does not always show two clearly separated steep jumps. State what additional data are needed to interpret the shape. [2]

3 Exam-style questions

3.1 Sketch four pH–volume curves for 25.0 cm³ of 0.100 mol dm^{−3} monoprotic acid receiving 0.100 mol dm^{−3} base: strong/strong, weak acid/strong base, strong acid/weak base and weak/weak. Label the axes and 25.0 cm³ equivalence amount. Show relative initial/final pH and the equivalence region; exact weak-species pH values are not required. [8]

3.2 A dibasic base B accepts two protons. 25.0 cm³ of 0.100 mol dm^{−3} B is titrated with 0.100 mol dm^{−3} HCl. Write each neutralisation step, calculate total volumes for the two equivalence amounts and explain the direction of the curve. [5]

3.3 A weak diprotic acid has sufficiently separated dissociations. On titration with strong base, first and second equivalence amounts occur at 20.0 and 40.0 cm³. Measured pH at 10.0 cm³ is 3.5; at 30.0 cm³ it is 8.0. Estimate pK_{a1} and pK_{a2} and explain the ratios used. Explain why these data do not by themselves select a colour indicator for either endpoint. [5]

Solutions

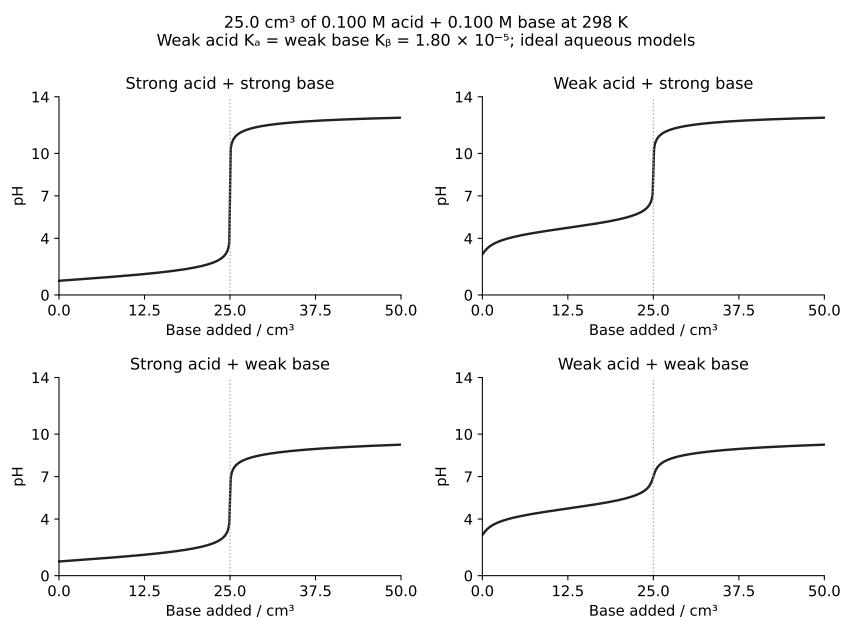
Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 Near 7; above 7; below 7 respectively. At weak-acid/strong-base equivalence, A^- accepts a proton from water to form OH^- , making the solution alkaline; or the conjugate acid of a weak base donates H^+ in the other case.

2.2 $n(H_2A) = 0.150 \times 0.0200 = 0.00300$ mol. First volume = $0.00300/0.100 = 0.0300$ dm³ = 30.0 cm³. Second total volume = 60.0 cm³ for two OH^- equivalents.

2.3 Similar dissociation constants can merge the stages, or a very weak later dissociation can give a poorly defined jump. Use the dissociation constants, concentrations and measured pH–volume data.

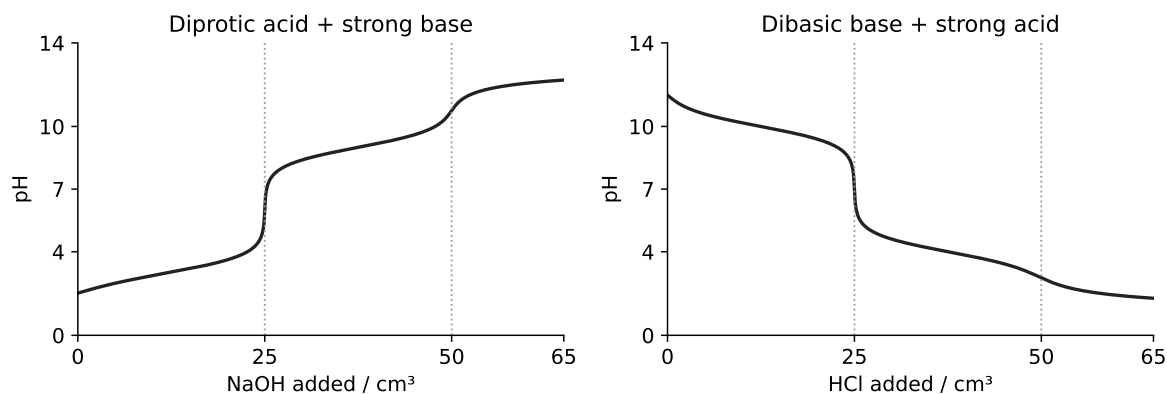
3.1 Completed model curves:



For each curve, B1 for appropriate start and excess-base region, B1 for equivalence-region shape/pH and correct 25.0 cm³ location (eight points total). Axes must state pH and added base volume. Weak/weak has a gradual region rather than the sharp strong/strong jump. Model weak-species constants are illustrative; an answer need not match their exact numerical pH.

3.2 $B + H^+ \rightarrow BH^+$ and $BH^+ + H^+ \rightarrow BH_2^{2+}$. Initial B amount is 0.00250 mol, so total HCl volumes are 25.0 and 50.0 cm³. Added acid lowers pH, giving the falling curve.

Two neutralisation stages: 25.0 cm³ of 0.100 M solute + 0.100 M titrant
 Illustrative separated dissociations, 298 K; dotted lines at 25 and 50 cm³



3.3 At 10.0 cm³ the first-stage acid/conjugate-base amounts are equal, so $\text{pK}_{\text{a}1} \approx 3.5$. At 30.0 cm³ the second-stage $\text{HA}^-/\text{A}^{2-}$ amounts are equal, so $\text{pK}_{\text{a}2} \approx 8.0$. Indicator choice needs its transition interval and the actual steep-region pH ranges; half-neutralisation pH alone does not give them.