

4.4.4 Acid–base data, buffer design and independent curve transfer

Name: _____ Class: _____ Date: _____ Total: **37 marks**

KEY WORDS buffer solution • conjugate acid

Objective

Use measured data to test an acid–base model, design a buffer and draw two-stage curves. All data are supplied illustrative models; questions and marking guidance are original.

1 Key knowledge and worked examples

A prediction is only as good as its assumptions. From measured pH, calculate $[H^+] = 10^{-pH}$ before checking the fraction of acid dissociated. Dilution increases this fraction for a weak acid; the small-dissociation approximation can fail before water becomes important.

■ Worked buffer design

For target pH 5.00 and $K_a = 2.00 \times 10^{-5} \text{ mol dm}^{-3}$, $[A^-]/[HA] = K_a/[H^+] = 2.00$. If the required final analytical total $[HA] + [A^-]$ is $0.120 \text{ mol dm}^{-3}$, write $[HA] + 2[HA] = 0.120$. Thus final HA is 0.0400 and A^- is $0.0800 \text{ mol dm}^{-3}$. These are final concentrations, not necessarily stock concentrations. Use $c_{stock}V_{stock} = c_{final}V_{final}$ separately for each component.

For a weak base B receiving strong acid, $B + H^+ \rightarrow BH^+$. While both remain, $[H^+] \approx K_a(BH^+)[BH^+]/[B]$. At half-equivalence their amounts are equal, so pH gives pKa of BH^+ , not of B. Added acid makes this curve fall.

2 Practice

2.1 Initially $0.100 \text{ mol dm}^{-3}$ HCl and monoprotic HA are separately diluted at constant temperature. Analyse the supplied measurements. Find the HCl pH rise at each dilution; compare HA with the half-log dilution rule. At 1000-fold dilution calculate $[H^+]$ and the percentage of HA dissociated. Explain why the small-dissociation assumption is then poor. Do not solve a quadratic. [6]

Dilution factor	HCl pH	HA pH
1	1.00	3.00
10	2.00	3.51
100	3.00	4.02
1000	4.00	4.57

2.2 Design 250.0 cm^3 of a buffer at pH 5.00 with final $[HA] + [A^-] = 0.120 \text{ mol dm}^{-3}$. $K_a = 2.00 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the two final concentrations. Only 40.0 cm^3 of acid stock and 60.0 cm^3 of salt stock will be used, then diluted to 250.0 cm^3 . Calculate both required stock concentrations. [6]

2.3 25.0 cm³ of 0.100 mol dm⁻³ weak base B is titrated with 0.100 mol dm⁻³ HCl. Measured pH at 12.5 cm³ is 9.25. Identify the conjugate acid, estimate its K_a and explain the equal-amount condition. Calculate the approximate pH at 20.0 cm³. Explain from the changing B:BH⁺ ratio why the central region buffers added acid. [6]

3 Exam-style questions

3.1 Draw two separate smooth pH–volume curves using all supplied points: 25.0 cm³ of 0.0600 mol dm⁻³ diprotic H₂A with 0.100 mol dm⁻³ NaOH, and the same amount of dibasic B with 0.100 mol dm⁻³ HCl. Mark the two equivalence amounts calculated from moles; identify the opposite directions. Exact vertical jumps are not required. [8]

Added titrant / cm ³	H ₂ A + NaOH pH	B + HCl pH
0	2.14	11.38
7.5	3.03	10.00
15.0	6.01	7.00
22.5	9.00	4.01
30.0	10.71	2.80
35.0	11.92	2.06

3.2 A student says: “Blood buffers remove every added acid permanently, and a food buffer kills microbes.” Use the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ pair to correct the blood claim with equations for added H^+ and OH^- . Explain why stable pH matters in cells and why buffering food can limit deterioration without proving sterility. State the capacity limit.^[5]

3.3 Propose a method to find K_a of a supplied pure monoprotic solid acid of known molar mass using a balance, volumetric flask and pH meter. Explain concentration determination, two pH-measurement controls, the calculation without assuming $c - x = c$ and one reason repeated readings alone cannot remove a systematic error.^[6]

Solutions

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

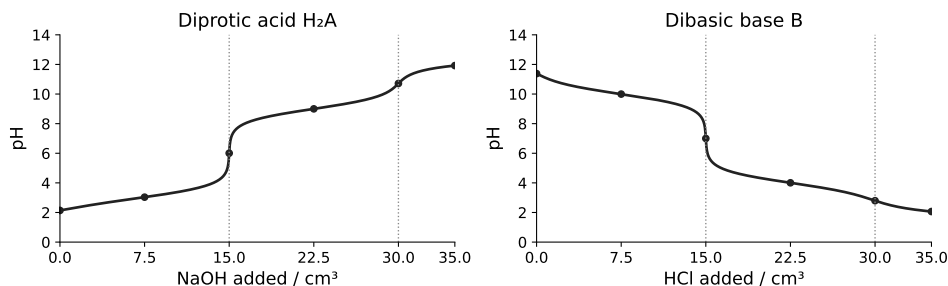
2.1 HCl rises by 1, 2 and 3 pH units relative to the original. HA rises by 0.51, 1.02 and 1.57, near but increasingly above the 0.50, 1.00 and 1.50 predictions. At factor 1000, $c = 0.100/1000 = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 10^{-4.57} = 2.69 \times 10^{-5} \text{ mol dm}^{-3}$. Dissociation is approximately $100[H^+]/c = 26.9\%$, too large to replace equilibrium HA by initial c . Water is not the main explanation at this pH.

2.2 $[H^+] = 10^{-5}$ and $[A^-]/[HA] = 2.00$. $3[HA] = 0.120$ gives final HA = 0.0400 and $A^- = 0.0800 \text{ mol dm}^{-3}$. Acid stock = $0.0400(250.0/40.0) = 0.250 \text{ mol dm}^{-3}$. Salt stock = $0.0800(250.0/60.0) = 0.333 \text{ mol dm}^{-3}$. Dilute the mixed aliquots to the stated final volume; do not add 250 cm^3 of water.

2.3 BH^+ is the conjugate acid. Initial B = 0.00250 mol; at 12.5 cm^3 H^+ added is 0.00125 mol, leaving equal B/ BH^+ . Hence $pK_a(BH^+) \approx 9.25$, $K_a = 10^{-9.25} = 5.62 \times 10^{-10} \text{ mol dm}^{-3}$. At 20.0 cm^3 , B = 0.000500 and $BH^+ = 0.00200 \text{ mol}$; $pH = 9.25 + \log_{10}(0.000500/0.00200) = 8.65$. Added acid converts B to BH^+ ; the ratio changes moderately while appreciable quantities of both remain, rather than leaving the added H^+ free.

3.1 Completed ideal-model curves through the supplied points:

25.0 cm³ of 0.0600 M solute + 0.100 M titrant, 298 K
Illustrative aqueous models; dotted lines mark 15.0 and 30.0 cm³



For each curve: B1 for axes/direction and appropriate end regions; B1 for plotting all six points with a smooth curve; B1 for first equivalence 15.0 cm³; B1 for second total equivalence 30.0 cm³. $n = 0.0600(0.0250) = 0.00150 \text{ mol}$; one and two titrant equivalents require 0.00150 and 0.00300 mol. Do not require a discontinuity: finite-concentration curves are continuous. Model constants are illustrative and supplied data, not a claim about every diprotic substance.

3.2 $HCO_3^- + H^+ \rightarrow H_2CO_3$; $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$. Limiting pH changes helps maintain enzyme activity/cell conditions. Food buffering can limit pH changes from microbial activity, but does not kill or exclude microbes and cannot alone establish safety/sterility. Added reagent consumes a component; once too little remains, capacity is exceeded. Blood also relies on respiratory/renal regulation, so buffering is not permanent unlimited acid disposal.

3.3 Weigh an accurately known mass m , dissolve completely, transfer/rinse quantitatively and make up to known volume V in a volumetric flask; $c = m/(MV)$ with V in dm³. Calibrate the meter with suitable standard buffers and maintain stated temperature/rinse the electrode between solutions. Measure equilibrium pH; $x = 10^{-pH}$, $[HA] = c - x$, $K_a = x^2/(c - x)$ when HA is the sole significant H^+ source. Repetition improves random scatter but does not correct a biased calibration, contaminated standard or wrong final volume. This is assessed method knowledge, not certification of practical performance.