

# Buffers, titration curves and indicators

## AP Chemistry · Worksheet answers

Each answer shows the reaction first, then the equilibrium step, which is the order that earns AP credit. Final values are in bold. Check your significant figures: pH values are given to two decimal places.

**Level:** AP Chemistry · **Curriculum:** AP Chem Unit 8

### Problem 1 Equal amounts of acid and base

$[A^-]/[HA] = 1$  and  $\log_{10}(1) = 0$ , so  $pH = pK_a = \mathbf{4.74}$ .

### Problem 2 Unequal buffer ratio

$pH = 4.74 + \log_{10}(0.40/0.20) = 4.74 + 0.30 = \mathbf{5.04}$ .

### Problem 3 Spot the buffers

A buffer needs a weak acid with its conjugate base, or a weak base with its conjugate acid.

(a) No: HCl is strong. (b) Yes. (c) Yes. (d) No: NaOH is strong. **Buffers: (b) and (c).**

### Problem 4 Choose a buffer pair

The best buffer has a  $pK_a$  within 1 unit of the target pH. 9.25 is only 0.05 away from 9.2, while 4.74 is 4.5 away. **Use  $NH_4^+/NH_3$ .**

### Problem 5 Equivalence volume

$n(HCl) = 0.0250 \times 0.100 = 2.50 \times 10^{-3} \text{ mol}$ .  $V(NaOH) = 2.50 \times 10^{-3} / 0.0500 = 0.0500 \text{ dm}^3$   
**= 50.0 cm<sup>3</sup>.**

### Problem 6 $pK_a$ from half-equivalence

1. At half-equivalence  $[HA] = [A^-]$ , so  $pK_a = \mathbf{4.76}$ .

2.  $K_a = 10^{-4.76} = \mathbf{1.7 \times 10^{-5}}$ .

### Problem 7 Ammonia buffer

$pH = pK_a + \log_{10}([NH_3]/[NH_4^+]) = 9.25 + \log_{10}(0.30/0.20) = \mathbf{9.43}$ .

**Problem 8 Adding base to a buffer**

1.  $n(\text{OH}^-) = 0.0050 \times 1.0 = 5.0 \times 10^{-3} \text{ mol}$ .
2.  $\text{HA} = 0.0200 - 0.0050 = 0.0150 \text{ mol}$ ;  $\text{A}^- = 0.0200 + 0.0050 = 0.0250 \text{ mol}$ .
3.  $\text{pH} = 4.74 + \log_{10}(0.0250/0.0150) = 4.96$ .

**Problem 9 Adding acid to a buffer**

1.  $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$ .
2.  $\text{NH}_3 = 0.025 - 0.0050 = 0.020 \text{ mol}$ ;  $\text{NH}_4^+ = 0.025 + 0.0050 = 0.030 \text{ mol}$ .
3.  $\text{pH} = 9.25 + \log_{10}(0.020/0.030) = 9.07$ .

**Problem 10 Making a buffer of given pH**

1.  $\log_{10}\text{ratio} = 4.90 - 4.74 = 0.16$ , so ratio = **1.45**.
2.  $n = 1.445 \times 0.200 = 0.289 \text{ mol}$ .
3.  $m = 0.289 \times 82.0 = 23.7 \text{ g}$ .

**Problem 11 Partial neutralisation**

1.  $n(\text{HA}) = 0.0500 \times 0.200 = 0.0100 \text{ mol}$ ;  $n(\text{OH}^-) = 0.0200 \times 0.100 = 2.00 \times 10^{-3} \text{ mol}$ .
2.  $\text{A}^- = 2.00 \times 10^{-3} \text{ mol}$ ;  $\text{HA} = 0.0100 - 0.0020 = 8.0 \times 10^{-3} \text{ mol}$ .
3.  $\text{pH} = 4.74 + \log_{10}(0.0020/0.0080) = 4.14$ .

**Problem 12 Before equivalence, strong acid**

$n(\text{H}^+) \text{ left} = 2.50 \times 10^{-3} - 2.00 \times 10^{-3} = 5.0 \times 10^{-4} \text{ mol}$  in  $45.0 \text{ cm}^3$ .  $[\text{H}^+] = 0.0111 \text{ mol/dm}^3$ , so  $\text{pH} = 1.95$ .

**Problem 13 Equivalence of ethanoic acid**

1.  $2.50 \times 10^{-3} \text{ mol}$  in  $50.0 \text{ cm}^3$  gives  **$0.0500 \text{ mol/dm}^3$** .
2.  $K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10}$ .
3.  $[\text{OH}^-] = \sqrt{(5.56 \times 10^{-10} \times 0.0500)} = 5.27 \times 10^{-6} \text{ mol/dm}^3$ ;  $\text{pOH} = 5.28$ ;  $\text{pH} = 8.72$ .

**Problem 14 Choose the indicator**

(a) The steep section runs from about pH 3 to 11, so **bromothymol blue** (or any of the three) works. (b) The equivalence point is near pH 8.7, which lies in phenolphthalein's range: **phenolphthalein**. Methyl orange would change colour too early.

**Problem 15 Comparing capacity**

1. A:  $\text{A}^- = 0.48 \text{ mol}$ ,  $\text{HA} = 0.52 \text{ mol}$ ;  $\text{pH} = 4.74 + \log_{10}(0.48/0.52) = 4.71$ .
2. B:  $\text{A}^- = 0.030 \text{ mol}$ ,  $\text{HA} = 0.070 \text{ mol}$ ;  $\text{pH} = 4.74 + \log_{10}(0.030/0.070) = 4.37$ .
3. Buffer A changed by 0.03 and B by 0.37. The more concentrated buffer A has the greater

capacity.

### Problem 16 Complete titration of methanoic acid

(a)  $x = \sqrt{(1.8 \times 10^{-4} \times 0.100)} = 4.243 \times 10^{-3} \text{ mol/dm}^3$  (4.2 % of 0.100, valid); pH = **2.37**.

(b) Half-equivalence: pH = pKa = **3.74**.

(c)  $[\text{HCOO}^-] = 0.0500 \text{ mol/dm}^3$ ;  $K_b = 5.56 \times 10^{-11}$ ;  $[\text{OH}^-] = 1.667 \times 10^{-6} \text{ mol/dm}^3$ ; pH = **8.22**.

(d) Excess  $\text{OH}^- = 5.0 \times 10^{-4} \text{ mol}$  in  $55.0 \text{ cm}^3 = 9.091 \times 10^{-3} \text{ mol/dm}^3$ ; pH = **11.96**.

### Problem 17 Derive the buffer equation

Rearrange:  $[\text{H}_3\text{O}^+] = K_a \times [\text{HA}]/[\text{A}^-]$ . Take  $-\log_{10}$  of both sides:  $\text{pH} = -\log_{10}K_a - \log_{10}([\text{HA}]/[\text{A}^-]) = \text{p}K_a + \log_{10}([\text{A}^-]/[\text{HA}])$ . With a ratio of 0.10:  $\text{pH} = 4.74 + \log_{10}(0.10) = 4.74 - 1 = \textbf{3.74}$ , one unit below pKa.

### Problem 18 Buffer from ammonia and HCl

1.  $9.00 = 9.25 + \log_{10}\text{ratio}$ , so ratio =  $10^{-0.25} = \textbf{0.562}$ .

2. Let  $n \text{ mol}$  HCl convert  $\text{NH}_3$  to  $\text{NH}_4^+$ :  $(0.0500 - n)/n = 0.562$ , so  $n = 0.0500/1.562 = \textbf{0.0320 mol}$ .

3.  $V = 0.0320/0.50 = \textbf{64.0 cm}^3$ .

### Problem 19 Unknown weak acid

1.  $n(\text{NaOH}) = 0.0315 \times 0.100 = 3.15 \times 10^{-3} \text{ mol} = n(\text{HA})$ ;  $c = 3.15 \times 10^{-3} / 0.0250 = \textbf{0.126 mol/dm}^3$ .

2.  $15.75 \text{ cm}^3$  is half of  $31.5 \text{ cm}^3$ , so pKa = **4.20** and  $K_a = 10^{-4.20} = \textbf{6.3} \times 10^{-5}$ .

3. Half the acid has been converted, so  $[\text{HA}] = [\text{A}^-]$  and  $\log_{10}(1) = 0$ .

### Problem 20 Capacity limit

1. The new pH is 4.64, so  $\log_{10}\text{ratio} = -0.10$  and ratio =  $10^{-0.10} = 0.7943$ .

2.  $(0.30 - n)/(0.30 + n) = 0.7943$ , so  $n = 0.30 \times (1 - 0.7943)/(1 + 0.7943) = \textbf{0.0344 mol}$ .

3.  $V = 0.0344 / 1.0 = \textbf{34 cm}^3$ .