Chem Factsbeet



www.curriculum-press.co.uk

Number 99

Why Students Lose Marks: A2 Acid Base Calculations

This Factsheet analyses students' answers to A2 exam questions on Acid-Base Equilibria. It aims to make you confident in

- knowing what the examiners expect from a good answer
- the type of questions you are likely to be asked
- common mistakes and misunderstandings

As you read the students answers to the questions and the comments, try to work out what the student should have done – using the hints and comments if necessary – before you read the correct answer. You will find the background knowledge needed is covered in Factsheets 25, 26, and 64.

To approach this type of question you will need to be able to:

- Identify acid-base behaviour by use of Brønsted Lowry Theory
- Recall (see below) definitions of pH, $K_{a, k_{w, v}} pK_{a, v} pK_{w}$ and calculate these
- Calculate the pH of solutions
- Sketch pH curves accurately.

1. $pH = -log_{10}[H^+]$

2. If the dissociation of a weak acid is represented by $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

then $K_a = \frac{[H^+(aq)] \times [A^-(aq)]}{[HA(aq)]}$

3.
$$pK_a = -log_{10}K_a$$

4.
$$K_w = [H^+(aq)] \times [OH^-(aq)] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^{\circ}\text{C}$$

5. $pK_w = -log_{10}K_w = 14 \text{ at } 25^{\circ}C$

Note: As seen in 1, 3 and 5, "p" is a general mathematical operator which means "take the log to base 10 of a number (e.g. K_a) and then take the negative of the answer"

In general there may be marks available for showing a clear method, and if an arithmetic slip has been made which the examiner can clearly see, then only one mark may be lost.

There are often marks available where an incorrect answer is the result of incorrect working in a previous part of the question. However, if the incorrect answer is based on an incorrect formula or incorrect science, then 'error carried forward' marks may not be available.

Rearranging equations and balancing equations are important skills and may be seen as part of the calculation. However, if a unit mark is available and the unit is correct (for a correct formula), then this mark will be awarded. Missing brackets or charges are penalised once in a question and result in the loss of one mark.

Example 1

In a buffer solution, the concentration of ethanoic acid is 0.250 mol dm^3 and the concentration of sodium ethanoate is 0.200 mol dm^3 .

The dissociation constant of ethanoic acid K_a has the value 1.74×10^{-5} mol dm⁻³ at 25°C.

$$K_a = \frac{[H^+] [CH_3 COO^-]}{[CH_3 COOH]}$$

Calculate the pH of the buffer solution.

Suppose the student rearranged the K_a expression to give

$$[\mathrm{H}^{+}] = \frac{[\mathrm{CH}_{3}\mathrm{COO}^{-}]}{\mathrm{K}_{3}[\mathrm{CH}_{3}\mathrm{COOH}]}$$

This is an incorrect rearrangement of the equation and means that the student can gain **no** marks, as the subsequent calculation would be based on incorrect science and would thus not be creditworthy. There is no unit mark available.

The correct rearranged equation is:

$$[H^{+}] = \frac{K_{a}[CH_{3}COO^{+}]}{[CH_{3}COO^{+}]}$$

$$= 1.74 \times 10^{-5} \times \frac{0.25}{0.20} = 2.175 \times 10^{-5} \text{ mol dm}^{-3} \qquad (1 \text{ mark})$$

One mark is awarded for the correct equation and a correct substitution gains one more mark.

 $pH = -log_{10}[H^+] = -log_{10}[2.175 \times 10^{-5}] = 4.663$

The pH is correctly calculated, but the degree of accuracy is too high, and the student loses this mark.

The pH should always be given to 2 decimal places, 4.66. (1 mark)

However, this type of error is only penalised once. If there were other calculations of pH in the same question and the final answers were also given to 3 decimal places, this would be condoned and only one mark lost for this type of error. Example 2

(i) The value of the acid dissociation constant for a weak acid HA at 298K is 1.74×10^{-5} mol dm⁻³.

Calculate the pH of a 0.350 mol dm⁻³ solution of HA at 298 K.

$$K_{a} = \frac{[H^{+}]^{2}}{[HA]}$$
(1 mark)

The student gains one mark for realising that $[H^+] = [A^-]$

This gives
$$[H^+] = \sqrt{\{(1.74 \text{ x } 10^{-5}) \times 0.350\}} \mod \text{dm}^{-3}$$
 (1 mark)

The student has correctly rearranged the equation and applied the approximation that, as the acid is weak, the acid which is dissociated can be counted as negligible, so the value of [HA] at equilibrium is taken to be 0.350 mol dm⁻³.

This approximation is expected, and the failure to use it would result in the student being faced with a difficult quadratic expression. One mark is given.

Suppose this gave $[H^+] = 6.09 \times 10^{-6} \mod dm^{-3}$

This would mean that the student has forgotten to square root his correct expression causing this mark to be lost. This should have been evident, as square rooting a calculation containing 10^{-5} or 10^{-6} will give an answer of the order of 10^{-3} so it is well worth checking that the answer is sensible.

The correct answer at this stage should be 2.468×10^{-3} mol dm⁻³. (1 mark)

However, if the student continues the calculation using $[H^+] = 6.09 \times 10^{-6} \text{ mol dm}^{-3}$

 $pH = -log_{10}[H^+] = -log_{10}[6.09 \times 10^{-6}] = 5.22$

One mark is still awarded as the pH calculation method is correct even though the answer is incorrect.

The correct answer should be

 $pH = -\log_{10}[H^+] = -\log_{10}[2.468 \times 10^{-3}] = 2.61$ (1 mark)

(ii) A mixture of this acid, HA and the sodium salt of this acid, NaA can be used to prepare a buffer solution. Calculate the concentration of A⁻ in the buffer solution if the pH is 3.65

Exam Hint: A common error in this type of calculation is to say that $[H^+] = [A^-]$. This is true only in a solution of the pure acid!

Suppose the student's first calculation step showed:

 $[H^+] = \log_{10} 3.65 = 0.562$

The student has incorrectly tried to calculate [H⁺] by taking the log of the pH and so loses this mark.

The correct answer should have been

$$[H^+] = 10^{-pH} = 10^{-3.65} = 2.239 \text{ x} 10^{-4} \text{ mol dm}^{-3}.$$

If the student's answer then continues:

$$[A^{-}] = \frac{K_{a}[HA]}{[H^{+}]}$$

$$= \frac{(1.74 \times 10^{-5}) \times 0.35}{0.562}$$

$$= 1.08 \times 10^{-5} \text{ mol dm}^{-3}$$
(1 mark)

The correct calculation should have been

$$[A^{-}] = \frac{(1.74 \times 10^{-5}) \times 0.35}{2.239 \times 10^{-4}}$$
(1mark)

$$= 0.0272 \pmod{\text{dm}^{-3}}$$
 (1mark)

The correct equation for calculating $[A^-]$ would gain one mark but, although the student correctly substitutes the (incorrect) value for $[H^+]$, this mark is lost because the value is based on a scientifically incorrect method for calculating the hydrogen ion concentration.

The correct formula has allowed the student to gain a follow through mark for his incorrect value for the concentration of A^- .

Example 3

At 40°C, the ionic product of water is 2.92 x 10^{-14} mol²dm⁻⁶ (i) Calculate the pH of pure water at 40°C.

Suppose the student wrote: $2.92 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6} = [\text{H}^+]$ and so $\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10} 2.92 \text{ x } 10^{-14} = 13.53$

The student has used the data given incorrectly having forgotten that $K_w = [H^+][OH^-]$ and for pure water $[H^+] = [OH^-]$.

Thus the square root of the value for K_w should be used to calculate $[H^+]$ and hence, the pH. Again, the student would gain no marks, as incorrect science gave an incorrect value for $[H^+]$, even though the correct formula for the pH is used. If the value for $[H^+]$ had been the result of incorrect use of the calculator but the correct use of the data then the mark for the calculation of pH would have been given and only one mark lost.

The correct response would be:

$$[H^+] = \sqrt{\{2.92 \times 10^{-14}\}} = 1.7088 \times 10^{-7} \text{ mol dm}^{-3} \quad (1 \text{ mark})$$

$$pH = -\log_{10}[H^+] = -\log_{10} 1.7088 \times 10^{-7} = 6.77 \qquad (1 \text{ mark})$$

The incorrect value obtained is that of a *strong* alkali, not pure water. This should have alerted the student to the fact that something had gone wrong! Always ask yourself, "is my answer reasonable?"

Remember: Unlike most K values you will meet, you are often expected to remember the value of K_w at 25 °C. i.e. 1.00 x 10⁻¹⁴ mol²dm⁻⁶

At 25 °C, the value of $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6}$ (ii) Calculate the pH at 25°C of

(a) a 0.140 mol dm⁻³ solution of potassium hydroxide.

This requires the use of K_w to link [OH⁻] to [H⁺] and hence, pH. It is also important to know that KOH is a strong base (fully ionised) which means that

9

(1 mark)

 $[OH^{-}] = [KOH] = 0.140 \text{ mol } dm^{-3}$

$$[\mathrm{H}^{+}] = \frac{\mathrm{K}_{\mathrm{w}}}{[\mathrm{OH}^{-}]} = \frac{1 \times 10^{-14}}{0.140} = 7.143 \times 10^{-14} \,\mathrm{mol}\,\mathrm{dm}^{-3} \qquad (1 \,\mathrm{mark})$$

One mark is gained for the correct use of K_w

 $pH = -\log_{10} [H^+] = -\log_{10} (7.143 \times 10^{-14}) = 13.15$ (1 mark)

The correct value for pH given to the correct degree of accuracy gains another mark.

(b) The solution formed when 45 cm³ of this solution of potassium hydroxide is mixed with 50 cm³ of a 0.115 mol dm⁻³ solution of hydrochloric acid.

Suppose the student's answer begins:

Moles OH⁻ used: = $\frac{V \times C}{1000} = 45 \times 10^{-3} \times 0.140 = 6.30 \times 10^{-3}$ (1 mark)

Moles H⁺ used:

 $= \frac{V \times C}{1000} = 50 \times 10^{-3} \times 0.115 = 5.75 \times 10^{-3}$ (1 mark) Since H⁺ and OH⁻ react 1:1

the excess moles of OH- in the resultant mixture

 $= 6.30 \times 10^{-3} - 5.75 \times 10^{-3}$ = 5.50 \times 10^{-4} (1 mark)

The student gains three marks, one for each correct moles calculation and one for the correct excess moles.

It is important to realise that the rest of the calculation is the same as part (a) because, in effect, you are dealing with a solution of potassium hydroxide with added potassium chloride.

Suppose the student's answer continued with:

 $K_{w} = 1.00 \times 10^{-14} \text{ mol}^{2}\text{dm}^{-6} = [\text{H}^{+}] [\text{OH}^{-}]$ $[\text{H}^{+}] = \frac{1.00 \times 10^{-14}}{5.50 \times 10^{-4}} = 1.818 \times 10^{-11} \text{ mol dm}^{-3}$

So $pH = -log_{10}[H^+] = -log_{10} 1.818 \times 10^{-11} = 10.74$

This is incorrect because the student has used "moles" instead of "mol dm⁻³" for [OH⁻]. This is a common error! The student should have realised that the excess moles of KOH were present in 95 cm⁻³ of solution which allows [OH⁻] to be calculated.

Two of the final three marks are lost but one follow through mark for the (incorrect) pH value is gained.

The correct solution should have been:

 $\begin{bmatrix} OH^{-} \end{bmatrix} = 5.50 \times 10^{-4} \times 1000 \div 95 \qquad (1 \text{ mark}) \\ = 5.789 \times 10^{-3} \text{ mol dm}^{-3} \qquad (1 \text{ mark}) \\ \end{bmatrix}$

$$[H^+] = \frac{1 \times 10^{-14} \text{ mol dm}^{-3}}{5.789 \times 10^{-3}} = 1.727 \times 10^{-12}; \text{ pH} = 11.76 \text{ (1 mark)}$$

If the volume is wrong the 4th mark is lost.

If the subtraction is missing from the calculation of the excess moles, then only the 1^{st} 2^{nd} and 4^{th} marks can be gained.

If the 1000 is missing then the $1^{st}\ 2^{nd}\ 3^{rd}\ 4^{th}$ and 6^{th} marks can be gained.

If the excess is used as acid, then the 1^{st} , 2^{nd} 4^{th} and 6^{th} marks can be gained.

If the excess is used as acid and the volume is not used, then the 1^{st} and 2^{nd} marks only can be gained.

Minor errors, such as missing square brackets or charges may be condoned in an otherwise correct calculation, and full marks given.

Question 4

Acid-base indicators can be represented as HIn. In aqueous solution: $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$

The pH is related to pK_{In} , the dissociation constant for the indicator equilibrium, by the equation

$$pH = pK_{In} + \log_{10} \frac{[In^{-}]}{[HIn]}$$

For bromothymol blue $K_{In} = 1 \times 10^{-7}$ mol dm⁻³

Calculate the pH of a solution in which $[In^-] = [HIn]$ for bromothymol blue.

Suppose a student's answer showed

 $pH = pK_{In} + 1$; $pH - 1 = pK_{In} = 7$; pH = 8

The student has forgotten to take the log of one so loses the first mark

The incorrect value for the pH loses the second mark. A correct response would have been:

$$log_{10} \frac{[In^{-}]}{[HIn]} = 0 \quad and therefore \ pK_{In} = pH \quad (1 \text{ mark})$$

$$pH = 7 \quad (1 \text{ mark})$$

Question 5

The change in pH as a 0.0550 mol dm⁻³ solution of potassium hydroxide is added to 30 cm³ of a solution of ethanedioic acid gives a titration curve which has two equivalence points.

When the second equivalence point is reached, a total of 36.7 cm³ of the 0.0550 mol dm⁻³ potassium hydroxide has been added. Calculate the concentration of the ethanedioic acid solution.

The student begins with:

Moles of OH⁻ added = $(36.7 / 1000) \times 0.0550 = 2.0185 \times 10^{-3}$ (1 mark)

which is correct and gains one mark.

The answer then continues:

Thus moles of ethanedioic acid present = 2.0185×10^{-3} Thus the concentration of ethanedioic acid = $2.0185 \times 10^{-3} \times (1000 / 30)$ = 0.0673 mol dm⁻³

This is incorrect because the student has failed to recognise that the ratio of hydroxide to acid at the second end point is 2:1 and so does not halve the moles of OH⁻.

Although the student follows through correctly, there is no follow through mark available and the student loses the final two marks.

The final answer should have been:

Thus moles of ethanedioic acid present = $2.0185 \times 10^{-3} / 2 (1 \text{ mark})$ = 1.009×10^{-3}

 $[H_2C_2O_4] = 1.009 \times 10^{-3} \times (1000 / 30) = 0.0336 \text{ mol dm}^{-3}(1 \text{ mark})$

Question 6

Using a burette, a 0.235 mol dm⁻³ solution of sodium hydroxide was added to 30cm³ of a 0.180 mol dm⁻³ solution of ethanoic acid.

Calculate the pH at 298K of the solution in the flask at the following points:

(i) before any sodium hydroxide had been added
(ii) after 10.0 cm³ of sodium hydroxide had been added
(iii) after 50 cm³ of sodium hydroxide had been added

The value of the acid dissociation constant for ethanoic acid is $K_a = 1.74 \times 10^{-5}$ at 298K.

The student's response begins:

(i) $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ (1 mark)

Stating the fundamental equation gains one mark and realising that $[H^+] = [CH_3COO^-]$ gains another mark.

Thus
$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$
 (*) (1 mark)

The first mark would not have been awarded had the student jumped straight to the approximation (*) which is commonly used for such calculations. It is always a good idea to state fundamental equations even if you are not too sure how to use them! They are often credited in the mark scheme.

The student then continues:

 $[H^+] = 1.74 \times 10^{-5} \times 0.180 = 3.132 \times 10^{-7}$ pH = 6.50

However, the student fails to square root and also gives an incorrect power of ten in his value. Both marks for this section are lost.

The nearly neutral pH should have alerted the student to the errors.

The correct response should have been:

 $\begin{array}{ll} [H^{*}] &= \sqrt{\{1.74 \times 10^{.5} \times 0.180\}} &= 1.770 \times 10^{.3} \mbox{ mol dm}^{.3} & (1 \mbox{ mark}) \\ pH &= 2.75 & (1 \mbox{ mark}) \end{array}$

(ii) The student's response to part (ii) begins:

Moles of NaOH added = $(10 / 1000) \times 0.235 = 2.35 \times 10^{-3}$ (1 mark)

Moles of CH₃COO⁻ formed = 2.35×10^{-3} (1 mark)

Original moles of $CH_{3}COOH = (30 / 1000) \times 0.180 = 5.40 \times 10^{-3}$ (1 mark)

Moles of CH₂COOH left = $(5.40 - 2.35) \times 10^{-3} = 3.05 \times 10^{-3}$ (1 mark)

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

This does not gain credit because the student assumes that only a weak acid is present, rather than an acidic buffer solution, and attempts to solve the problem in a similar way to the first part.

This gives $[H^+] = \sqrt{\{1.74 \times 10^{.5} \times 3.05 \times 10^{.3}\}} = 2.304 \times 10^{.4} \text{ mol dm}^{.3}$ pH = 3.64

The student fails to notice that, according to his / her calculations, the addition of NaOH has made the solution more acid! This cannot be correct.

The calculation should have been done as follows:

$$[H^{+}] = K_{a} \times \frac{[CH_{3}COOH]}{[CH_{3}COO^{-}]}$$
(1 mark)
= 1.74 × 10⁻⁵ × $\frac{3.05 \times 10^{-3} \times (1000 / 40)}{2.35 \times 10^{-3} \times (1000 / 40)}$
= 2.258 × 10⁻⁵ mol dm⁻³ (1 mark)

$$pH = 4.65$$
 (1 mark)

(iii) The student's answer to (iii) begins Total moles of NaOH added = $(50 / 1000) \times 0.235 = 1.175 \times 10^{-2}$ (1 mark)

Therefore
$$pOH = 1.93$$

And pH = 14.00 - 1.93 = 12.07

The student has failed to allow for the fact that some of the sodium hydroxide has been used by reaction with the acid. The number of moles of NaOH is excess needed to be calculated.

Also, he / she has forgotten that the excess NaOH is now present in a new total volume of 30 + 50 = 80 cm³ which has to be used when calculating its concentration.

This results in no further marks being gained.

The correct solution would have continued:

Excess moles of NaOH = $(11.75 - 5.40) \times 10^{-3} = 6.35 \times 10^{-3}$ (1 mark)

| Total volume of mixture = $30 + 50 = 80 \text{ cm}^3$ | (1 mark) |
|---|----------|
| | |

Therefore
$$[OH^{-}] = 6.35 \times 10^{-3} \times (1000 / 80) = 0.0794$$
 (1 mark)

Therefore pOH = 1.10

or
$$[H^+] = 10^{-14} \div 0.0794 = 1.259 \times 10^{-13} \text{ mol dm}^{-3}$$
 (1 mark)

Therefore
$$pH = 12.90$$
 (1 mark)

(1)

(3)

(2)

(2)

(2)

Practice Questions

1. Citric acid acts as an antioxidant used in food. If it is used together with its sodium salt, it can also act as an acidity regulator.

(a) Assuming citric acid behaves as a monoprotic acid when in aqueous solution, the equation for its dissociation is: $RCO_2H + H_2O \Rightarrow RCO_2^- + H_3O^+$ Give the expression for K_s for citric acid.

- (b) If K_a for citric acid at 298K is 7.4×10^4 mol dm⁻³ calculate the pH of lemon juice which contains citric acid at a concentration of 0.250 mol dm⁻³.
- (c) Calculate the pH of a buffer solution containing $0.250 \text{ mol dm}^{-3}$ of citric acid and $0.450 \text{ mol dm}^{-3}$ of sodium citrate. (3)
- 2. (a) Calculate the pH of 0.150 mol dm⁻³ potassium hydroxide solution at 25°C. (K_{u} at 25°C is 1.0×10^{-14}) (2)
 - (b) 100 cm³ of $0.100 \text{ mol dm}^{-3}$ potassium hydroxide solution was added to 100 cm^{-3} of $0.200 \text{ mol dm}^{-3}$ ethanoic acid.
 - (K_a for ethanoic acid at 25°C is 1.80×10^{-5} mol dm⁻³.)
 - (i) Find the concentration of ethanoic acid in the mixture.
 - (ii) Calculate the concentration of potassium ethanoate in the mixture.

2

(iii) Calculate the pH of the mixture at 25°C.

Answers

1. (a)
$$K_a = \frac{[RCO_2^{-}][H_3O^+]}{[RCO_2H]}$$
 (1) allow [H⁺] for [H₃O⁺]

(b)
$$7.4 \times 10^4 = \frac{[H_3O^+]^2}{0.25}$$
 (1) allow $[RCO_2H] = [H_3O^+]$
 $[H_3O^+] = \sqrt{\{0.25 \times 7.4 \times 10^4\}}$
 $= \sqrt{\{1.85 \times 10^4\}}$
 $= 0.0136 \text{ mol dm}^3$ (1)
 $pH = 1.87$ (1) must be given to 2 d.p. or
this mark is lost.

Correct answer with no working (1) only for part (b).

(c)
$$7.4 \times 10^{-4} = \frac{0.45 \times [\text{H}_3\text{O}^+]}{0.25}$$
 (1)
 $[\text{H}_3\text{O}^+] = \frac{0.25}{0.45} \times 7.4 \times 10^{-4}$
 $= 0.556 \times 7.4 \times 10^{-4}$
 $= 4.1 \times 10^{-4} \text{ mol dm}^{-3}$ (1)
 $\text{pH} = 3.39$ (1)

If not 2 d.p. then one mark lost **unless** this type of error was penalised in part (b).

| (a) | $[OH^{-}] = 0.100 \text{ mol } dm^{-3}$ | |
|-----|---|-------|
| | $[H^+] = 10^{-13} \text{ mol dm}^{-3}$ | (1) |
| | pH = 13.00 | (1) |
| | Must have working for 2 | marks |

(b) (i) Half the ethanoic acid will have reacted and the total volume of the mixture will have doubled.

Therefore the concentration is a quarter of the original. (1) (This can be shown by a suitable calculation.)

Concentration of ethanoic acid = 0.05 mol dm^{-3} (1)

(ii) Number of moles of salt produced = 0.01 (1) Therefore concentration of salt = 0.05 mol dm⁻³ (1)

(iii) pH = pK_a + log₁₀
$$\frac{[salt]}{[acid]}$$
 (1)

This mark can be gained either for correct equation or correct substitution

$$pH = -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{0.05}{0.05}$$

$$pH = 4.74$$
(1)

Acknowledgements: This Factsheet was researched and written by Christine Collier. Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher. ISSN 1351-5136