

A Second Year blog on Acids and Bases: 30th March 2019

*(This is a revision note written purely for Second Year 'A' Level students who are just about to take their final exams. This is a biggish subject, and you do **need to understand Sections A and B**, and some Examination Boards require you to understand Section C. Stop when you have done Section A and B, and ask yourself: have I done enough revision of Organic Chemistry and of Modern Analytical Techniques. If you have not, then move on and revise Organic and MAT. Only if you know your OC and MAT inside out, then carry on with Section C. The principles underlying Section C are the same as those in Section B therefore, in theory, if you know how to do the calculations in Section B you can do those in Section D. In practice however, that is not the case.)*

- I have taught both the OCR and the Edexcel 'A' Level Syllabi, but I do not know what every Examination Board in the UK requires, therefore in this note I shall cover the titrations of
 - a Strong Acid against a Strong Base
 - a Weak Acid against a Strong Base, and
 - a Strong Acid against a Weak Base.
- The calculations in Section A are mainly revision (of how to perform the calculations involved in titrating one substance against another, and then in performing the calculations for the pH values as the titration proceeds), but you may have covered the calculations in Sections B and C so long ago that you now need reminding of the complicated procedures involved – and they **are** moderately complicated procedures.
- Please make sure that you understand why you need an ICE table for Sections B and C, and then make sure that you know the 12 tips that I give you on page 3.
- This note is **by no means** an easy read. You may therefore want to switch off your mobile phone, make a huge pot of coffee, lock your bedroom door and leave strict instructions that you are not to be disturbed for three hours (or if necessary even longer). However, once you have been through and understood the calculations in this note, then you will have cracked wide open a large portion of the 'A' Level Maths in Chemistry – and also in your first year at Med School if you want to go on and do Medicine. (The Mathematics involved in this note do require you to be numerate¹, and this note will stand you in good stead if you want to do any sort of Science Degree such as Medicine/Physics/Engineering/Computer Science/or Chemistry – or you just need a high grade in Chemistry in order to get into the University of your choice.)

¹ My youngest adopted son appears not to know the first thing about either grammar or syntax, and is not (what I would call) a Mathematician, but he is **numerate** – and that is possibly how he got his PhD, and is now an extremely competent clinician.

I *started* to write this note to explain Question 12 from the Edexcel paper (6CH04_01_rms_20160817) of 2016, but I have widened it to be a **much more** fundamental commentary on some of the Maths that underlie Titrations (a subject that comes up again and again in the ‘A’ Level exams).

Actually, in essence, the Maths in this note is just GCSE Maths with a bit of logs thrown in. In other words, the Maths itself is fairly easy, but it is *complicated* (i.e. not difficult, but fiddly). Any ‘A’ Level student should be able to eat the Maths in here for breakfast. **The ‘trick’ lies not in the Maths, but in making sure that you know what you are doing at each step of the analysis.** In other words you do not need to be a mathematician to do this sort of stuff, **but you DO need to be logical/methodical/tidy in setting out your written workings/and you must have a clear understanding of where you want to go, and what you have to do to get there.**

I do not pretend that the stuff in this note is easy, but it is immensely satisfying when you get to the end of each set of calculations. If you can master the calculations involved in calculating the changing pH values during a titration for either a Weak Acid or a Weak Base, then **you have a very good brain (any brain that can do COMPLICATED Chemistry IS a very good brain)**, and (provided that you have a nice personality and you are willing to work hard) then you have every chance of having a successful professional career – and if you then meet the right person to stand shoulder-to-shoulder with you through your life, then you also have every chance of having an exceedingly happy life.

In this note, I am going to take you through the calculations that you need to make at each stage of the procedure – and I am going to give you a very **thorough** grounding in the Maths and in the calculations that are involved. If you are not competent at Maths, then you will not be able to do Computing/Maths/Engineering/or get into ‘the City’ – but you should also think very carefully about wanting to become a Doctor/Dentist/Pharmacist/Radiologist/Optician/etc.

If you get your arithmetic wrong, then you can easily KILL a patient!

If you become an Investment Banker and you lose millions of pounds in a deal, then that is just tough luck on your employer; but, if you kill even **one** of your patients through carelessness or because you do not know that the difference between a pH of 1 and a pH of 7 is a

**ONE MILLION-FOLD increase in the concentration of the H^+ ions in the acid
then you WILL kill one of your patients
(and if your pH is wrong by a factor of even just “1”, then you WILL kill your patient).**

If you kill a patient, it will sit heavily on your conscience for the rest of your life. In anything to do with Medicine, it is people’s lives that you are dealing with! The same is true if you are designing a bridge/or a building/or whatever. I am not here to teach you Maths. I am here to teach you Chemistry, but please do make sure that you do understand the Maths that I am teaching you. It really is rather important.

Towards the end of your first year I told you that if you wanted to get into the University of your choice, and especially if you wanted to read Computing/Maths/Engineering/Law/or wanted to get into ‘the City’, then you ought to do a spreadsheet for the changing pH values in a titration. The spreadsheet exercise is one of the most valuable things that you can do as a scientist to start making your transition from an ‘A’ Level student to becoming an undergraduate. The calculations that you will need to make are all contained in this note (and all that I am going to do herein is to **use the calculations that you WILL be examined on at ‘A’ Level, nothing more than that – just ‘A’ Level stuff**).

These are the ‘signposts’ that you will need throughout the whole of this note

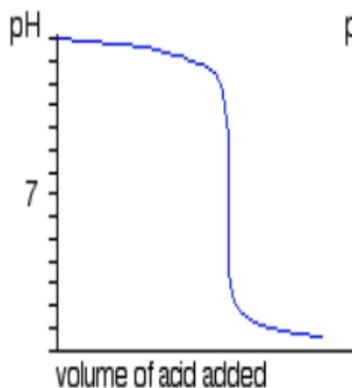
- 1) The p of X = $-\log_{10}(\text{the concentration of X})$, therefore the **pH of a solution = $-\log_{10}([\text{H}^+])$** , but
- 2) for a base please remember you will need to use **pH = 14.0 – pOH**.
- 3) Concentration = Number of moles ÷ Volume of the solution, or **C = N ÷ V in dm³**
- 4) If you are dealing with a Weak Acid or a Weak Base, then you **MUST** use an ICE table.
- 5) For reversible reactions that are at dynamic equilibrium at a given temperature, K_a and K_b are all about concentrations (raised to the power of their stoichiometric ratios). You must therefore construct an ICE table for **concentrations** (or for moles which you must then divide by volumes). **Your answer will therefore be wrong if you forget to put your Water in the reversible reaction equation** (because you must divide moles by the same number of volumes on each side of the reversible reaction equation).
- 6) Please remember that in an ICE table you **ignore the change** in $[\text{H}_2\text{O}]$. $[\text{H}_2\text{O}]$ is very small ($K_w = 1 \times 10^{-14}$) and you can ignore $\Delta[\text{H}_2\text{O}]$. **However, we are not ignoring the “[H₂O] = 1.0”**. We **cannot** ignore the “1.0” because then we would have two lots of the volume as the DIVISOR on one side of an equation and only one lot of volume on the other side – and then ALL our calculations would be wrong thereafter. K_a and K_b are about **concentrations**, and **C = N ÷ V**.
- 7) Therefore keep track of the number of moles of the Titrant that you are adding to the Analyte, **and** keep track of your volumes (because K_a and K_b are all about **concentrations**).
- 8) If the unknown variable in an ICE table is designated as “z”, then you **can** resolve the value of “z” by using a *quadratic equation* – but that will involve you in a fair amount of number crunching and (usually) it will **not** make any difference to the value of the pH that eventually emerges. In the **vast** majority of cases, when solving for the value of “z²” you can ignore any numbers that involve “–z” or “+z”, **but you cannot ignore any numbers that involve “times z” and “÷ z”**. That makes the arithmetic much easier and doing so makes no difference to the final value of the pH (which is normally given to just ONE decimal place anyway).
- 9) **$K_a \cdot K_b = K_w = 1 \times 10^{-14}$** , and taking the log of both sides of that equation then **$\text{p}K_a + \text{p}K_b = 14.0$**
- 10) A titration curve is ‘S-shaped’ and it has three parts to it
 - one third is where either the acid or the base is being neutralised (i.e. if it is an acid/base titration)
 - a central point where the two reacting substances (the titrant and the analyte) have exactly reacted with each other, and this point is called the Equivalence Point, and
 - the last bit, where the **concentration** of the second substance i.e. the Titrant (which is being dripped from the burette into the conical flask), *as measured in the conical flask* is getting larger and larger.
- 11) When dealing with either a Weak Acid or a Weak Base, then by the very definition of “weakness” you are involved in reactions that reach a position of dynamic equilibrium when only a small proportion of their “acidity” or their “basicity” has been released and, to calculate your pH values, you must then use the Henderson-Hasselbalch equation which for a Weak Acid
“ $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ ” says
$$\text{pH} = \text{p}K_a + \log_{10} \left\{ \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} \right\}$$

Concentration of the SALT
Concentration of the ACID
- 12) **Whenever you add a Weak Acid to Water you get H^+ ions, and when you add a Weak Base to Water you get OH^- ions.**
- 13) At half the volume of the volume at the equivalence point, the pH of a Weak Acid is equal to its $\text{p}K_a$. This stems from an analysis of the mid-point of the Henderson-Hasselbalch equation (Chapter 9 of the Year 2 book)

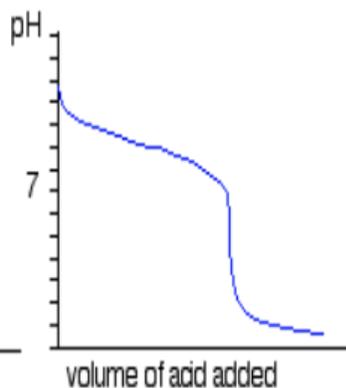
and this is what Q12/Edexcel/2016 was all about – **and what all acid/base titrations are about.**

- Jim Clark in his excellent website “chemguide” shows the graphs thus, and please take careful note of the difference in the shapes of the graphs.

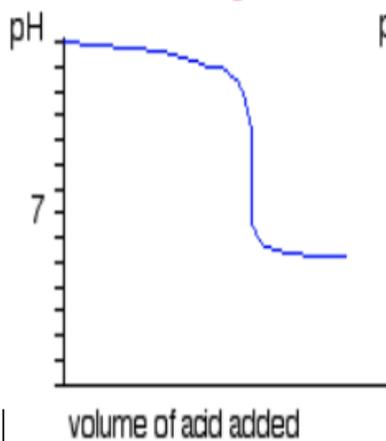
A strong acid is being added to a strong base



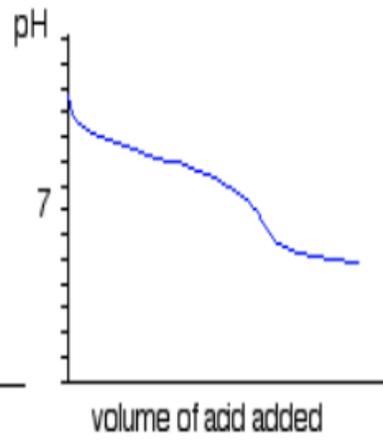
A strong acid is being added to a Weak Base



A Weak Acid is being added to a strong base



A Weak Acid is being added to a Weak Base



NB The first part of the graph on the right should be much flatter than it has been drawn.

- As you can see, the starting pH in all four situations is **above 7** (that means that Mr Clark is starting with a base in his conical flask and is measuring the pH of the solution in his conical flask throughout the titration).
- Mr Clark is **dripping an acid into an alkali** and he is giving you the pH value of the contents of the conical flask during the course of the titration (which is why the *starting* pH is above 7).
- Mr Clark could just as well have started his titration with his acid in the conical flask – and then each pH would have started with a low value and it would have risen during the course of the titration.
- **OK, I have given you enough background to start us off – so let us start looking at the Maths that will allow us to calculate the changing pH values during the titration – and please remember that both the singular and the plural for the SI unit for moles is “mol”.**

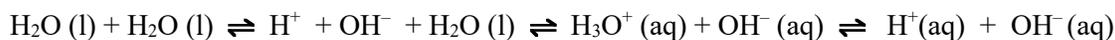
Section A: an analysis of the Maths for Strong Acids/Strong Bases

A1) Strong Acid vs a Strong Base at the Equivalence Point

- Please keep in mind that a Strong Acid will exactly neutralise a Strong Base at the Equivalence Point (EP) therefore at the EP, the pH of the solution will be simply that for pure Water = 7.0 at 298K. **The pH at the EP states the log of the concentration of the H⁺ ions resulting from the dissociation of pure Water** (and please remember that $K_w = 1 \times 10^{-14} = [\text{H}^+] \cdot [\text{OH}^-]$, therefore $[\text{H}^+] = 1 \times 10^{-7}$).
- This must be so, because at the EP all the H⁺ ions from the Strong Acid will have been neutralised by the OH⁻ ions from the Strong Base, therefore the only H⁺ ions and OH⁻ ions that there are in the solution will be those from the pure Water.

The Equilibrium Ionic Product of Water Constant, K_w, using H₂O ⇌ H⁺ + OH⁻

- The reaction equation for the dissociation of pure water is



therefore the K_c for pure Water at a given temperature is

$$K_c = \frac{[\text{H}^+(\text{aq})] [\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O} (\text{l})]}$$

and just as with K_a, since [H₂O (l)] is just a number (which at 298K is 55.5), the Equilibrium Ionic Product of Water Constant, K_w, at a given temperature can be and is defined as

$$K_c \cdot [\text{H}_2\text{O} (\text{l})] = K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]$$

- The K_c for pure water at 298K is almost exactly 1.8×10^{-16} therefore (ignoring the units)

$$K_w = K_c \cdot 55.5 \approx 1.8 \times 10^{-16} \times 55.5 \approx 1 \times 10^{-14} \quad \text{at 298K}$$

and, since the stoichiometric ratio of $\text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})$ is 1 : 1 : 1, $[\text{H}^+] = [\text{OH}^-]$, and $[\text{H}^+(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$, and $[\text{OH}^-(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$, therefore

$$K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] \approx (1 \times 10^{-7} \text{ mol dm}^{-3}) \cdot (1 \times 10^{-7} \text{ mol dm}^{-3})$$

$$\begin{array}{l} \text{or} \quad [\text{H}^+]^2 = [\text{OH}^-]^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}, \\ \text{and} \quad [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3} \end{array}$$

- The p of X is the $-\log_{10}(X)$, therefore

$$\text{the pH of pure Water at 298K} = -\log_{10}([\text{H}^+]) = -\log_{10}(1 \times 10^{-7}) = 7.0$$

Please go over the steps in this logic until you really do understand it.

- At the Equivalence Point for the titration of a **Strong Acid against a Strong Base**, the H^+ ions from the acid and the OH^- ions from the base have exactly neutralised each other, and the pH of the solution is therefore **just that of the dissociated H^+ ions from pure Water = 7.0** .

A2) Strong Acid vs Strong Base at the commencement of the titration

- Let us (for the sake of the arithmetic) assume that we are titrating **50 cm³ of 0.5 mol dm⁻³ HCl** in a conical (Erlenmeyer) flask against **200 cm³ of 0.2 mol dm⁻³ NaOH** in a burette (burettes in labs are not are that big, but this is about learning how to do the Maths and not about doing the actual experiment), and that we are monitoring the pH of the solution in the conical flask. (I have deliberately chosen different strengths for the acid and the base so that you *have* to do the arithmetic rather than be able to just guess what the answers are going to be. (If you have set up a spreadsheet, then it will be child's-play to change the concentrations and see the resulting change in pH values. Once you have set a spreadsheet up, it will be child's play to do **ANYTHING**. **That is the beauty of a computer!**)

NB The p of X = $-\log_{10}(\text{X})$, therefore

**the pH of a solution will be $-\log_{10}(\text{the concentration of the } \text{H}^+ \text{ ions in the solution})$
i.e. $-\log_{10}([\text{H}^+])$**

therefore to calculate the pH of the solution at any point in a titration we need to calculate the concentration of the H^+ ions in the solution at that point, and please remember that
Concentration = Number of moles \div Volume of the solution, or $C = N \div V$ in dm³ .

A2.1) The pH at the start before any NaOH has been added

- $C = N \div V$ in dm³ and we were given that for HCl, $C = 0.5 \text{ mol dm}^{-3}$
but $\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$ or $\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
therefore the mole reaction ratio is 1: 1 : 1 ,
therefore $[\text{H}^+] = [\text{HCl}] = 0.5 \text{ mol dm}^{-3}$
and **pH = $-\log_{10}(0.5) = 0.3010 \approx 0.3$** .

A2.2) The pH when 30 cm³ of NaOH have been added

- We now need to ask:
 - a) how many moles of OH^- are there in 30 cm³
 - b) how many moles of H^+ ions will they neutralise
 - c) how many moles of H^+ ions were there originally
 - d) how many moles of H^+ ions are there left
 - e) what is the volume of the solution at this point
 - f) what is the $[\text{H}^+]$ now, and
 - g) what is the pH now?

and the answers to these questions are as follows

(and remember that all your calculations must be in **dm³** and **not** in cm³)

- $N = C \times V$ in dm^3 , therefore $N = 0.2 \text{ mol dm}^{-3} \times (30 \div 1000) \text{ dm}^3 = 0.006 \text{ mol}$ or $6.0 \times 10^{-3} \text{ mol}$.
- The mole reaction ratio for HCl and NaOH is 1 : 1, therefore N of H^+ neutralised = $6.0 \times 10^{-3} \text{ mol}$.
- N of H^+ originally = $C \times V$ in dm^3 , therefore $N = 0.5 \text{ mol dm}^{-3} \times (50 \div 1000) \text{ dm}^3 = 0.025 \text{ mol}$
- N of H^+ ions left = $(0.025 - 0.006) \text{ mol} = 0.019 \text{ mol}$
- V after 30 cm^3 have been added to $50 \text{ cm}^3 = (30 + 50) \text{ cm}^3 = 80 \text{ cm}^3 = 0.08 \text{ dm}^3$
- The $[\text{H}^+]$ now is given by $C = N \div V$ in $\text{dm}^3 = 0.019 \text{ mol} \div 0.08 \text{ dm}^3 = 0.2375 \text{ mol dm}^{-3}$, and please remember that you omit the units when it comes to taking the log
- therefore $\text{pH} = -\log_{10}([\text{H}^+]) = -\log_{10}(0.2375) = 0.6243 \approx 0.6$.

- It is now very clear that after adding 30 cm^3 of NaOH the pH value has risen from 0.3 to 0.6, and you should not find this surprising because the more **alkali** that you add to an acid, the larger will the pH value become! The pH of the solution when all the 200 cm^3 of NaOH have been added will be somewhere near the pH of the NaOH itself (but we will come to that in due course).

A2.3) The pH when 125 cm^3 NaOH have been added

- We now need to ask the same set of questions as we did before, so I shall repeat them
 - how many moles of OH^- are there in 125 cm^3
 - how many moles of H^+ ions will they neutralise
 - how many moles of H^+ ions were there originally
 - how many moles of un-neutralised H^+ ions are there left
 - what is the $[\text{H}^+]$ now, and therefore
 - what is the pH now?

and the answers to these questions are as follows

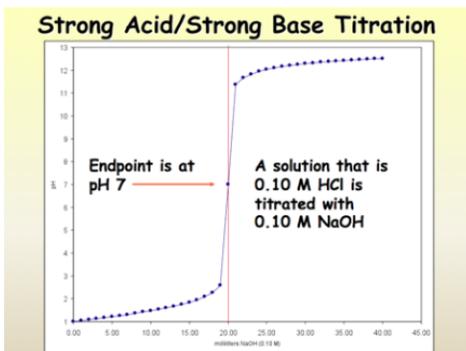
- $N = C \times V$ in dm^3 , therefore $N = 0.2 \text{ mol dm}^{-3} \times (125 \div 1000) \text{ dm}^3 = 0.025 \text{ mol}$.
- The mole reaction ratio for HCl and NaOH is 1 : 1, therefore N of neutralised H^+ ions = 0.025 mol.
- N of H^+ originally = $C \times V$ in dm^3 , therefore $N = 0.5 \text{ mol dm}^{-3} \times (50 \div 1000) \text{ dm}^3 = 0.025 \text{ mol}$
- N of H^+ ions left = $(0.025 - 0.025) \text{ mol} = 0.0 \text{ mol}$.

- All the H^+ ions have been exactly neutralised at this point, therefore we are at the **Equivalence Point** (the bit where the pH value goes shooting upwards almost in a straight line), and at the point of exact neutralisation, the only H^+ ions in the solution are those from the dissociation of pure Water, and earlier I did for you the calculation to show that

the pH of pure Water at 298K = $-\log_{10}([\text{H}^+]) = -\log_{10}(1 \times 10^{-7}) = 7.0$

- However, this is true only for the titration of Strong Acids and Strong Bases.** For
 - a **Strong Acid** with a **Strong Base**, the Equivalence Point will always be at 7.0 at 298K
 - a **Strong Acid** with a Weak Base, the Equivalence Point **will always be < 7.0** at 298K
 - a Weak Acid with a **Strong Base**, the Equivalence Point **will always be > 7.0** at 298K (and in a moment we will see why this is so).
- Having reached the Equivalence Point, any NaOH that is added will take us into the top half of the S-shaped titration curve. In Andy Allan's graph below, the strengths of the Acid and the Base are

different from the ones that I am using in this note, but all that the graph is meant to do is to remind you of the shape of the curve.



An S-shaped titration curve

Source: Andy Allan's sciencegeek.net

The next statement is **VERY** important. We have neutralised ALL the H^+ ions in the strong acid therefore to calculate the pH of the solution in the conical flask we must now

- i) start calculating the concentration of the OH^- ions in the conical flask, then
- ii) we must calculate the **pOH value** from the $[OH^-]$, and then
- iii) we must use the fact that **pH + pOH = 14.0** to find the pH of the solution in the flask.

A2.4) The pH when a further 30 cm^3 (i.e. 155 cm^3 in all) of NaOH have been added

- We are now in the Alkaline part of the curve and we need to ask a new set of questions
 - a) how many moles of OH^- are there in 155 cm^3 of NaOH
 - b) how many moles of OH^- ions did the H^+ ions neutralise
 - c) how many moles of OH^- ions are there which have **not** been neutralised
 - d) what is the volume of the solution in the flask now
 - e) what therefore is the concentration of the un-neutralised OH^- ions
 - f) what is the pOH now, and therefore
 - g) what is the pH now?

The answers to these questions are as follows

- a) N of OH^- in 155 cm^3 of NaOH = $C \times V$ in dm^3 , therefore $N = 0.2\text{ mol dm}^{-3} \times (155 \div 1000)\text{ dm}^3 = 0.031\text{ mol}$.
- b) There were 0.025 mol of H^+ ions in the HCl and they neutralised 0.025 mol of OH^- ions.
- c) Therefore N of un-neutralised OH^- ions = $(0.031 - 0.025)\text{ mol} = 0.006\text{ mol}$ of OH^- ions.
- d) The volume in the flask now is $(50 + 155)\text{ cm}^3 = 0.205\text{ dm}^3$.
- e) C of OH^- ions in the flask = $N \div V$ in $\text{dm}^3 = 0.006\text{ mol} \div 0.205\text{ dm}^3 = 0.02927\text{ mol dm}^{-3}$.
- f) The pOH therefore = $-\log_{10}(0.02927) = 1.5336$, and
- g) pH = $14.0 - 1.5336 \approx 12.5$.

- As the titration has progressed, the pH has risen as follows **0.3 / 0.6 / 7.0 / 12.5**.
- We can now ask the questions
 - What will the pH be when all the 200 cm^3 of NaOH have been added?
 - What was the pH of the NaOH to start with?

A2.5) What will the pH be when all the 200 cm³ of NaOH have been added?

- We now need to ask the questions
 - a) how many moles of OH⁻ are there in 200 cm³ of NaOH
 - b) how many moles of OH⁻ ions did the H⁺ ions neutralise
 - c) how many moles of OH⁻ ions are there which have **not** been neutralised
 - d) what is the volume of the solution in the flask now
 - e) what therefore is the concentration of the un-neutralised OH⁻ ions
 - f) what is the pOH now, and therefore
 - g) what is the pH now?

The answers to these questions are as follows

- a) N of OH⁻ in 200 cm³ of NaOH = C x V in dm³, therefore N = 0.2 mol dm⁻³ x (200 ÷ 1000) dm³ = 0.040 mol.
- b) There were 0.025 mol of H⁺ ions in the HCl.
- c) N of H⁺ originally = C x V in dm³, therefore N of OH⁻ left = (0.040 – 0.025) mol = 0.015 mol of OH⁻ ions.
- d) The volume in the flask now is (50 + 200) cm³ = 0.250 dm³.
- e) C of the OH⁻ ions in the flask = N ÷ V in dm³ = 0.015 mol ÷ 0.250 dm³ = 0.06 mol dm⁻³.
- f) The pOH therefore = -log₁₀(0.06) = 1.2218, and
- g) pH = 14.0 – 1.2218 ≈ **12.8**.

A2.5) What was the pH of the original NaOH?

pH of a base = (14.0 – its pOH), therefore what was its pOH?

pOH = -log₁₀([OH⁻] ions)

Since NaOH (aq) → Na⁺ (aq) + OH⁻ (aq), and the mole reaction ratio is 1 : 1 : 1, then the C of OH⁻ ions = [OH⁻] = C of NaOH = **0.2 mol dm⁻³** because that is what we were told, then -log₁₀([OH⁻]) = -log₁₀(0.2) ≈ 0.7

therefore pH of the NaOH that we used = 14.0 – 0.7 = **13.3**.

- **That is it. That is the Maths for calculating the changing pH value when a Strong Acid is titrated against Strong Base.**

OK, what about Weak Acids and bases? Well, they are a different kettle of fish, so let us now look at them!

Section B: an analysis of the Maths for Weak Acids/Strong Bases

- When a Weak Acid or a Weak Base is involved you **CANNOT** use the same analysis as in Section A! (NB Most Organic Acids i.e. Carboxylic Acids are weak ones.)
- You have to use a **totally** different form of analysis altogether. You must use something called an ICE Table, where the initials stand for
 - I Initial
 - C Change
 - E at Equilibrium.
- The reason why you need a different form of analysis is that, by definition, a Weak Acid and a Weak Base dissociate hardly any H⁺ ions in the case of Weak Acids (or OH⁻ ions in the case of Weak Bases) before they reach a position of dynamic equilibrium. Now this brings Le Chatelier's Laws into the equation, therefore this note is not only going to remind you of stuff that you need to know about acids and bases, but I hope that it will also remind you that you need to revise all of the stuff about Chemical Equilibria. (In fact, the exams that are coming up in 10 weeks' will examine you on **everything** that you have learnt in the last two years, so make sure that you are on top of your Revision.)
- For the most part, for the Weak Acids that you will encounter at 'A' Level, just 1 molecule in every 100,000 molecules of the acid will be dissociating a proton at its position of dynamic equilibrium i.e. 1 x 10⁻⁵, and quite often the proportion may be as little as 1 x 10⁻¹⁰. In other words, **Weak Acids dissociate hardly any protons at all before they reach their position of dynamic equilibrium.** Please remember that the Equilibrium Constant, K, does not change for a given temperature – but if you change the temperature, then the value of K will change. **K is temperature dependent.** (That came up in a recent exam paper.)
- The next thing that I am about to tell you is unbelievably important. When you write your reaction equations for an ICE table, you **MUST** write your Water into the equation. If you do not do so, then you will get the wrong answer. In a reaction that is in dynamic equilibrium, at the point where the rate of the forward reaction exactly equals the rate of the backward reaction, then the reaction is said to be in dynamic equilibrium at that temperature. We write such **reversible reactions** as



and there is a constant K_c which expresses the relationship

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{at equilibrium at a given temperature}^2.$$

NB The equation denotes the “concentration” (in square brackets) of the relevant product or reactant raised to its stoichiometric number, where a/b/c/and d are the stoichiometric numbers for the substances A/B/C/and D respectively e.g. [D]^d is the *concentration* of the product D raised to the power of “d”. The concentrations of the **PRODUCTS** are the **numerators** and the concentrations of the **REACTANTS** are the **denominators** (i.e. the concentrations of the **PRODUCTS** are divided by the concentrations of the **REACTANTS**).

² The symbol “[X]” means “the **Concentration** of the substance X”, where C = N ÷ V, where “N” is the number of moles and “V” is the volume in cubic decimetres (dm³), and C is thus expressed in mol dm⁻³.

- Now, this is the bit on which you must focus:
 - to get the **concentrations** of the substances involved in the reaction at dynamic equilibrium you must divide the Number of moles of each substance by the Volume of the whole solution at that point;
 - and if you do not have the same volume **on BOTH sides of the equation**,
 - then your numerator will be divided by two lots of the Volume (let's say 50 cm³), but
 - your denominator will be divided by only one lot of that volume,
and your answer will then be wrong.
- If you look at the relationship for K_c again, you will see what I am saying viz.

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{at equilibrium at a given temperature}$$

- The way to avoid this problem is to do your ICE table in **CONCENTRATIONS** (as I will do in the calculations that follow in this note), or the alternative is to do the ICE table in moles **but not to forget to include your WATER in your calculations.**

NB This is a revision note, so I am going to assume that you have read the whole of the Year 2, Inorganic Chemistry book and that you are therefore already familiar with the basics of what I am telling you now – and please remember that you will be examined on this in your exams in 10 weeks' time. ICE tables are a part of the UK 'A' Level Syllabus. All that I am doing in this note is to go through the Maths behind the calculations for the changing pH values.

B1) The initial pH value of the Weak Acid in the titration of a Weak Acid against a strong base

- For this next bit of Section B I am going to analyse what happens when you titrate **70 cm³** of a Weak Acid, Hydrocyanic Acid or "Prussic Acid" HCN, whose **concentration is 1.25 mol dm⁻³** and whose **K_a = 6.0 x 10⁻¹⁰** against a strong base NaOH whose concentration (here) is **0.25 mol dm⁻³** (but I could titrate *any* Weak Acid HA against my chosen Strong Base of any concentration).

YOU CANNOT JUST TAKE THE LOG OF 1.25 mol dm⁻³ to get the pH! THIS IS A WEAK ACID!

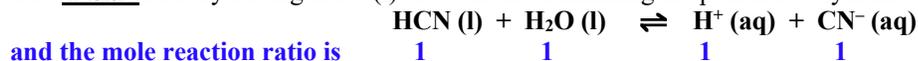
- A Strong Acid will dissociate almost completely in Water, therefore the concentration of the H⁺ ions will be exactly the same as the concentration of the acid itself.**
- However, for a weak acid, in order to find the concentration of the H⁺ ions, you MUST find out what happens at the point of DYNAMIC EQUILIBRIUM, therefore look at**

$$\text{HCN (l)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{CN}^- \text{ (aq)} \quad \text{(at the given temperature).}$$
- Please examine that equation very carefully so that you understand what it is saying viz. that at equilibrium, a liquid molecule of HCN has dissociated an H⁺ ion and the H⁺ ion has then piggy-backed a ride on the Water molecule that was nearest to it.
- HCN is a Weak Acid therefore you must use an ICE table to track the change in concentration of the H⁺ ions.**
- In an ICE table [H₂O] is taken to be "1", and when you add the liquid HCN to the liquid Water, to begin with before dissociation starts to occur, **[H⁺] = 0, and [CN⁻] = 0** (see the table overleaf). The trick is then to assume that at dynamic equilibrium **[H⁺]** which will also = **[CN⁻] = z** .

NB I use "z" instead of "x" as my unknown variable because I want to avoid confusion with the mathematical symbol "x" that is used for multiplication.

PLEASE READ THIS PAGE VERY CAREFULLY

You **MUST** start by adding HCN (l) to water and examining the position at dynamic equilibrium



To find the $[\text{H}^+]$ at dynamic equilibrium, we **MUST** use an ICE table. In this table “z” represents the concentration of H^+ and because the mole reaction ratio of this reaction is 1:1:1:1, $[\text{H}^+] = [\text{CN}^-]$. The **change** in the concentration of pure Water is so small ($K_w = 1 \times 10^{-14}$) that its contribution to the concentration of H^+ ions in the solution can be ignored in this calculation. (NB **The CONCENTRATION of Water in Water = “1”**, and **you are not ignoring the “1”, but you are ignoring the change in “1” i.e. you are ignoring $\Delta\text{H}_2\text{O}$** , but many textbooks do not explain this clearly.)

Concentrations of		HCN	H ₂ O	H ⁺	CN ⁻
I	(for Initial)	1.25	1.0	0	0
C	(for Change)	-z	ignore	+z	+z
E		<hr/>			
	(for at Equilibrium)	(1.25-z)	1.0	z	z

$$K_a = \frac{[\text{H}^+].[\text{CN}^-]}{[\text{HCN}] \times 1} = 6.0 \times 10^{-10} = \frac{z \cdot z}{(1.25-z)} = \frac{z^2}{(1.25-z)}$$

$$\text{Therefore } z^2 = (6.0 \times 10^{-10}) \times (1.25-z) = 1.25 (6.0 \times 10^{-10}) - z \cdot (6.0 \times 10^{-10})$$

Now, “ $z \cdot (6.0 \times 10^{-10})$ ” is such a small number that we can ignore its contribution to the value of ‘ z^2 ’. (We don’t have to. We could solve for “z” using a quadratic equation, but through long experience chemists have found that doing so makes hardly any difference at all to the value of the resulting pH.)

$$\begin{aligned} \text{Therefore } z^2 &\approx 1.25 (6.0 \times 10^{-10}) = 7.5 \times 10^{-10} \\ \text{and } z &\approx 2.739 \times 10^{-5} \end{aligned}$$

NB Can you remember that on page 7 I told you that “For the most part, for the Weak Acids that you will encounter at ‘A’ Level, just 1 molecule in every 100,000 molecules of the acid will be dissociating a proton at its position of dynamic equilibrium i.e. 1×10^{-5} , and quite often the proportion will be only 1×10^{-10} ”. **Well now you can see that for yourself!**

- The pH of this Weak Acid at this temperature is therefore $-\log_{10}(2.739 \times 10^{-5}) \approx 4.6$, and I can check that my maths has probably **not** gone wrong because I know that Weak Acids have a pH of about 3-7, and my 4.6 figure falls in this range. (Please always do mental checks on your arithmetic to make sure that you have not typed something stupid into your clever calculator.)
 - Up to now, all that we have done is to calculate the pH of the Weak Acid (here HCN) when it has reached dynamic equilibrium at a given temperature (let’s say RTP where $T = 298\text{K}$). We have as yet not added any NaOH at all.
 - I have so far used an ICE table to get the pH value for my Weak Acid (HCN), but for the next step I will need to use a Henderson-Hasselbalch equation for a ‘buffer’ solution. I will have to leave it to you to read Chapters 8 and 9, of Year 2 Inorganic Chemistry on Buffer solutions and Henderson-Hasselbalch equations, but I will remind you that buffer solutions are made up of a mixture of either
 - i) a **WEAK acid plus a fully dissociated (strong) salt of that Weak Acid**, or
 - ii) a **WEAK base plus a fully dissociated (strong) salt of that Weak Base**and where the cations in the salts of the acids are usually either Sodium or Potassium, and the anions in the salts of the bases are often chlorides
- and, it is also the case that
a buffer solution will exist where the concentrations of an acid and its conjugate base are approximately equal (and it certainly will when they **are** equal).

- The other thing that I must remind you of is that at dynamic equilibrium (at a given temperature),

$$\text{HA (aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{A}^- \text{(aq)} \quad [\text{where } \text{H}^+ \text{(aq)} = \text{H}_3\text{O}^+ \text{(aq)}]$$

there will be an equilibrium constant K_a such that

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

and by rearranging the above equation we get

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

- If we now take the logs of both sides of this equation to the base 10 we obtain

$$\log_{10}[\text{H}^+ \text{(aq)}] = \log_{10}[K_a] + \log_{10} \left\{ \frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]} \right\}$$

and if we now multiply the whole equation by “-1” we get

$$-\log_{10}[\text{H}^+ \text{(aq)}] = -\log_{10}[K_a] + -\log_{10} \left\{ \frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]} \right\}$$

which gives $\text{pH} = \text{p}K_a - \log_{10} \left\{ \frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]} \right\}$ $\frac{\text{Concentration of the ACID}}{\text{Concentration of the SALT}}$

and this equation is most often re-arranged as

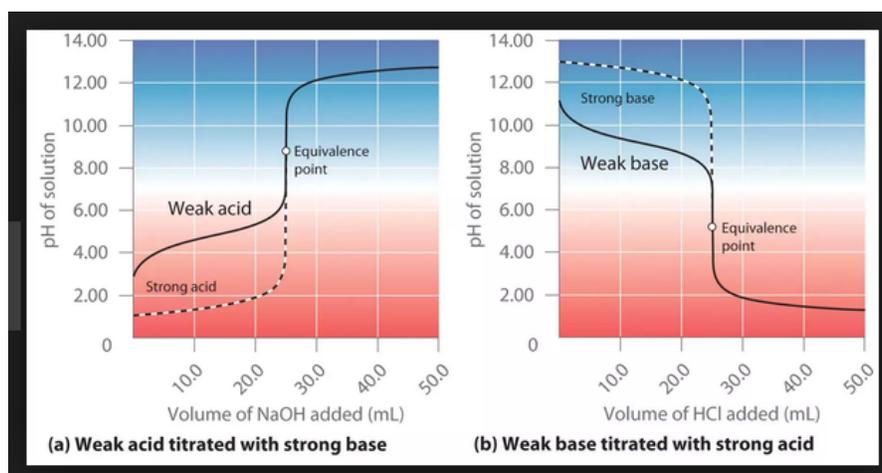
$$\text{pH} = \text{p}K_a + \log_{10} \left\{ \frac{[\text{A}^- \text{(aq)}]}{[\text{HA (aq)}]} \right\} \quad \frac{\text{Concentration of the SALT}}{\text{Concentration of the ACID}}$$

- Now let us look at the equation for the reaction of HCN (aq) with NaOH (aq).
- After the addition of some NaOH to the HCN,



- If the HCN has not been fully neutralised, then the HCN that is left will reach a new position of dynamic equilibrium and (since we are given K_a and can therefore calculate $\text{p}K_a$), all that we need to do now is to find the concentration of the salt $[\text{A}^-]$ and the concentration of the acid $[\text{HA}]$ i.e. the concentrations of the salt and the acid after the addition of the NaOH, and then we can calculate the pH from the Henderson- Hasselbalch equation that I have quoted above.
- Let us do that.

- I will start by reminding you of the shape of the titration curve for the titration of a Weak Acid against a Strong Base – and you will see that the starting point of the curve in the titration that we are doing is not the 0-3 of a strong acid but 3-7 of a Weak Acid (and from the calculation that we have already done, our starting pH in this particular titration that we are doing today is 4.6).



Source: Chemistry LibreTexts

B2) The pH value after the addition of 100 cm³ of NaOH

- Let me remind you that we are dealing with
 - **70 cm³** of a Weak Acid, Hydrocyanic Acid or “Prussic Acid” HCN
 - whose **concentration is 1.25 mol dm⁻³** and
 - whose **K_a = 6.0 x 10⁻¹⁰** (*actually, I suspect that the figure is probably nearer 6.2 x 10⁻¹⁰, but that will not affect the methodology of the calculation*)
 - reacting with a strong base NaOH whose concentration (here) is **0.25 mol dm⁻³**
 - and that we have got to the point in the calculation where we are going to use the Henderson-Hasselbalch equation for a Buffer Solution viz.

$$\text{pH} = \text{pK}_a + \log_{10} \left\{ \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} \right\} \quad \frac{\text{Concentration of the SALT}}{\text{Concentration of the ACID}}$$

NB We know that we have a Buffer Solution because

- we have a Weak Acid HCN, and
 - we have a fully dissociated strong salt of that Weak Acid (NaCN), and
 - now all that we need to find is [A⁻] and [HA], and then we can calculate the pH value after the addition of 100 cm³ of NaOH.
 - Please remember that for a Weak Acid $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ at dynamic equilibrium.
- Before you turn to the next page, I would like to remind you that a pH is all about **the concentration of H⁺ ions in a given volume** – but here we are adding 100 cm³ of NaOH (say by adding it from a burette to a conical flask, therefore we have changed the volume), so how are we going to construct our ICE table? Please think about it before turning to the next page.

- We therefore need to ask:
 - how many moles of OH⁻ are there in **100 cm³** of NaOH
 - how many moles of H⁺ ions will they neutralise
 - how many moles of H⁺ ions were there originally
 - how many moles of H⁺ ions are there left
 - what is the volume of the solution at this point
 - what is the [H⁺] now
 - what is the pH now?

and the answers to these questions are as follows

(and remember that all your calculations must be in **dm³** and **not** in cm³)

- $N = C \times V$ in dm³, therefore N of NaOH = 0.25 mol ~~dm⁻³~~ x (100 ÷ 1000) ~~dm³~~ = 0.025 mol.
- From the equation **HCN (aq) + NaOH (aq) ⇌ H₂O (l) + NaCN (aq)** we know that the mole reaction ratio is 1 : 1 : 1 : 1, therefore N of H⁺ neutralised = 0.025 mol.
- N of H⁺ originally = C x V in dm³, therefore N = 1.25 mol ~~dm⁻³~~ x (70 ÷ 1000) ~~dm³~~ = 0.0875 mol
- Therefore N of H⁺ ions left = (0.0875 – 0.025) mol = 0.0625 mol
- V after 100 cm³ have been added to 70 cm³ = (100 + 70) cm³ = 170 cm³ = 0.17 dm³

We can see all that in the following table, where [H₂O] = 1, and the change in the number of H⁺ ions from the dissociation of pure Water is so small that its contribution can be ignored, and K_a was given as **K_a = 6.0 x 10⁻¹⁰**.

NB Please remember that the concentration of Water molecules in Water always = “1”.

Moles*	[HCN]	[NaOH]	[H ₂ O]	[NaCN]
I (for Initially)	0.0875	0.025	1.0	0
C (for Change)	-0.025	-0.025	ignore	+0.025
E (for at Equilibrium)	0.0625	0.0	1.0	+0.025

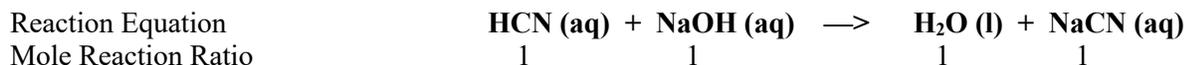
* We can leave everything in moles because dividing the two lots of moles on the left of the equation and the two lots of moles on the right of the equation by 0.17 dm³ will not affect the arithmetic at all.

$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log_{10} \left\{ \frac{[\text{A}^- (\text{aq})]}{[\text{HA} (\text{aq})]} \right\} = -\log_{10}(6.0 \times 10^{-10}) + \log_{10} \left(\frac{0.025}{0.0625} \right) \\
 &= 9.2218 - 0.3979 \\
 &\approx 8.824 \text{ (say 8.8)}.
 \end{aligned}$$

- Can you remember that on page 7 I told you that for
 - a **Strong Acid** with a **Strong Base**, the Equivalence Point will always be at 7.0 at 298K
 - a **Strong Acid** with a **Weak Base**, the Equivalence Point **will always be < 7.0** at 298K
 - a **Weak Acid** with a **Strong Base**, the Equivalence Point **will always be > 7.0** at 298K,
 well, we have **not** even got to the Equivalence Point and the pH value is already above 7.0.

B3) The pH value after the addition of 350 cm³ of NaOH (This will be the Equivalence Point, EP)

- Please look at the reaction equation below and you will see that in this reaction we have (i) a Weak Acid, HCN, and (ii) the fully dissociated strong salt of that Weak Acid, NaCN – therefore we have here a Buffer Solution, and therefore to calculate the concentrations involved and the pH value, we use an ICE table and the Henderson-Hasselbalch equation.



- The number of moles of HCN in 70 cm³ of 1.25 mol dm⁻³ HCN = 0.0875 mol, therefore we need 0.0875 mol of NaOH to exactly neutralise the HCN.
- $V = N \div C$, therefore the V of NaOH to give 0.0875 mol = $0.0875 \text{ mol} \div 0.25 \text{ mol dm}^{-3} = 0.35 \text{ dm}^{-3}$
Therefore the addition of 350 cm³ of NaOH will exactly neutralise the 70 cm³ of 1.25 mol dm⁻³ HCN.
- At the EP, all the H⁺ ions will have been neutralised (other than for the miniscule amount, $N = 1 \times 10^{-7}$, arising from the dissociation of pure Water), and **the big thing that will determine the pH of the resulting solution will be the concentration of the CN⁻ ions** (and a base is anything that accepts a proton, therefore CN⁻ is a proton acceptor), because the CN⁻ will react with the Water in the solution and drive off OH⁻ ions. **NaCN itself has no OH⁻ ions in it, but when it reacts with Water it generates a sufficient number of OH⁻ ions to influence the pOH value and hence the pH value of the solution.**
- The equation that will drive this next reaction is therefore

$$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{CN}^- + \text{H}^+ + \text{OH}^- \rightleftharpoons \text{OH}^- + \text{HCN}$$
and we need to know the concentration of the CN⁻ ions. (NB [H₂O] = 1.)
- We therefore have to construct an ICE table for this reaction where
 - the number of moles of NaCN, as calculated above = 0.0875 mol
 - the volume of the solution is now (70 + 350) cm³ = (420 ÷ 1000) dm³ = 0.42 dm³
 - therefore [NaCN] = $N \div V \text{ in dm}^3 = (0.0875 \text{ mol}) \div (0.42 \text{ dm}^3) = 0.2083 \text{ mol dm}^{-3}$

Concentration	[CN ⁻] from the NaCN	[H ₂ O]	⇌	[OH ⁻]	[HCN]
I (for Initial)	0.2083	1.0		0	0
C (for change)	-z	ignore		+z	+z
E (for at Equilibrium)	(0.2083-z)	1.0		z	z

- Please note that up to now we have been dealing with a reaction for the dissociation of H⁺ ions that is driven by the dynamic Equilibrium Constant K_a, **but now we are dealing with a reaction for the dissociation of OH⁻ ions that is driven by the dynamic Equilibrium Constant K_b!**
- We were not given K_b but we were given K_a, but we know that $K_a \times K_b = K_w = 1 \times 10^{-14}$
therefore we can calculate $K_b = (1 \times 10^{-14}) \div (6.0 \times 10^{-10}) = 1.6667 \times 10^{-5}$.
- We therefore now know that

$$K_b = 1.6667 \times 10^{-5} = \frac{z \cdot z}{(0.2083-z)} = \frac{z^2}{(0.2083-z)}$$

- Therefore $z^2 = (1.6667 \times 10^{-5}) \times (0.2083 - z) = 3.4722 \times 10^{-6} - z(1.6667 \times 10^{-5})$

and since $z \cdot 10^{-5}$ (i.e. 1 in 100,000) is so small that we can ignore it, we get

$$z^2 = 3.4722 \times 10^{-6} \quad \text{and} \quad z = 1.8634 \times 10^{-3} .$$

- $z = [\text{OH}^-]$ therefore $\text{pOH} = -\log_{10}([\text{OH}^-]) = -\log_{10}(1.8634 \times 10^{-3}) = 2.73$

for a base, the $\text{pH} = 14.0 - \text{pOH} = 14.0 - 2.73 \approx 11.3$.

- Therefore at the Equivalence Point for the titration of this particular Weak Acid (HCN) against a Strong Base (NaOH), the $\text{pH} = 11.3$ (quite a large amount above 7.0!) .

This is therefore the third time therefore that I will tell you that for

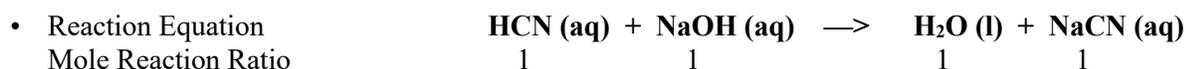
- a **Strong Acid** with a **Strong Base**, the Equivalence Point will always be at 7.0 at 298K
- a **Strong Acid** with a Weak Base, the Equivalence Point **will always be** < 7.0 at 298K
- a Weak Acid with a **Strong Base**, the Equivalence Point **will always be** > 7.0 at 298K,

and now we have an Equivalence Point with a pH value of 11.3 !

and I hope that everything is starting to fit together!

- Quite frankly, the Chemistry that I am teaching you here is not important. I am much more interested in showing you how powerful your brain is. **I want you to fall in love with your brain.** I promise you that if you have even a half-decent brain, then if you train it and use it, you will have a very successful career in whatever field you choose.

B4) The pH value after the addition of 360 cm³ of NaOH



and we want to know what the concentration of the OH⁻ ions are at this point in the titration because
pH = 14.0 - pOH

- Well, [OH⁻] will be determined by three factors
 - a) the OH⁻ ions from the un-neutralised NaOH that has been added to the HCN
 - b) the OH⁻ ions from the reaction of CN⁻ with the Water in the solution (as we saw just now), and
 - c) the OH⁻ ions from the dissociation of the pure Water (but as we saw earlier, we tend to ignore this because it makes hardly any difference to the final pH value because $K_w = 1 \times 10^{-14}$ and this is such a small number that it makes virtually no difference to the final answer).
- Any mathematician who is a stickler for perfection would take into account all **three** factors, but chemists tend not to do so because pH values are normally given to just one decimal point and the contribution of [H⁺] and of [OH⁻] from the pure Water will not alter the pH figure **except at the Equivalence Point for the titration of a Strong Acid against a Strong Base.**

- In this instance I am going to do the calculation first of all using
 - the OH^- ions from the un-neutralised NaOH that has been added to the HCN and then
 - the OH^- ions from the reaction of CN^- with the Water in the solution (as we saw just now), and then we can see whether (b) gives a different answer from (a). **My guess is that it will not do so.**

B4a) The pH value after the addition of 360 cm³ of NaOH looking at the OH⁻ ions given off by the un-neutralised NaOH that has been added to the HCN but ignoring the effect of the reaction of CN⁻ with Water³

- Let me remind you that we are dealing with 70 cm³ of a Weak Acid, Hydrocyanic Acid or “Prussic Acid” HCN, whose concentration is 1.25 mol dm⁻³ and whose $K_a = 6.0 \times 10^{-10}$ (but possibly nearer 6.2×10^{-10}) with a strong base NaOH whose concentration (here) is 0.25 mol dm⁻³
- From our earlier calculations we know that
 N of H^+ in HCN = $C \times V$ in dm³, therefore $N = 1.25 \text{ mol dm}^{-3} \times (70 \div 1000) \text{ dm}^3 = 0.0875 \text{ mol}$
 and we can work out the number of moles in 360 cm³ of NaOH = $N = C \times V$ in dm³
 therefore N of $[\text{OH}^-]$ in 360 cm³ of NaOH = $0.25 \text{ mol dm}^{-3} \times (360 \div 1000) \text{ dm}^3 = 0.09 \text{ mol}$.
- The HCN will have neutralised 0.0875 mol of these 0.09 mol, therefore the number of moles of un-neutralised OH^- ions after adding 360 cm³ of Na OH = 0.0025 mol.
- We can therefore construct an ICE table and get

Moles	HCN	NaOH = OH^-	H ₂ O	NaCN = CN^-
I (for Initially)	0.0875	0.09	1	0
C (for Change)	-0.0875	-0.0875	ignore	+0.0875
	0.0	0.0025	1	0.0875

- The volume of the solution after adding 360 cm³ of NaOH = $(70 + 360) \text{ cm}^3 = 0.430 \text{ dm}^3$.
- Please remember that in the ICE table we are ignoring the change in “1.0”, because it is so small ($K_w = 1 \times 10^{-14}$). **We are not ignoring the “1.0”. We cannot ignore the “1.0” because then we would have two lots of the volume (i.e. 430 cm³) as the DIVISOR on the left hand side and only one lot of volume on the right hand side – and then ALL our calculations would be wrong thereafter. K_a and K_b are all about concentrations, and $C = N \div V$.**
- If for (B4a) we ignore the contribution of OH^- made by the reaction of CN^- and Water, then

$$[\text{OH}^-] = N \div V = 0.0025 \text{ mol} \div 0.43 \text{ dm}^3 = 5.814 \times 10^{-3} \text{ mol dm}^{-3}$$

therefore $\text{pOH} = -\log_{10}(5.814 \times 10^{-3}) = 2.2355$
 therefore $\text{pH} = 14.0 - 2.2355 \approx 11.8$.

³ Through a reversible reaction, H₂O dissociates a tiny amount of H^+ and OH^- ions, and the CN^- ion will react with an H^+ ion to form HCN. Anything that accepts a proton is a base, because a Brønsted-Lowry base is a proton acceptor, therefore CN^- is a base.

B4b) The pH value after the addition of 360 cm³ of NaOH looking at the OH⁻ ions generated by the un-neutralised NaOH that has been added to the HCN but this time allowing for the effect of the reaction of CN⁻ with Water

- Please remember that we are now going to take into account the OH⁻ ions that are produced when
 Reaction Equation $\text{CN}^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{OH}^- (\text{aq}) + \text{HCN} (\text{aq})$
 Mole Reaction Ratio $\quad 1 \quad \quad 1 \quad \quad 1 \quad \quad 1$
- From the table in (B4a), we can see that N of CN⁻ = 0.0875 mol
 therefore since $C = N \div V$ in dm³, $[\text{CN}^-] = 0.0875 \text{ mol} \div 0.43 \text{ dm}^3 = 0.2035 \text{ mol dm}^3$
- Now, since the CN⁻ is a Weak Base, then just as in (B3) we need to use an ICE table to calculate the concentration of the OH⁻ ions that have been dissociated when CN⁻ reacts with Water.
- From (B4a) at the bottom of page 18, we know that [OH⁻] from the NaOH = **5.814 x 10⁻³** mol dm⁻³
 therefore if we now also take into account the OH⁻ ions that are generated by the reaction of CN⁻ with Water, then we get

Concentration	[CN ⁻] from the NaCN	[H ₂ O]	[OH ⁻] from the NaOH	[HCN]
I (for Initial)	0.2035	1.0	0.005814	0
C (for change)	-z	ignore	+z	+z
E (for at Equilibrium)	(0.2035 - z)	1.0	(0.005814 + z)	z

NB Please remember that we are in the top half of this titration curve therefore we have first to calculate the pOH value in order to arrive at the pH value, and that in B3 we calculated that $K_b = (1 \times 10^{-14}) \div (6.0 \times 10^{-10}) = 1.6667 \times 10^{-5}$.

- We can now write $K_b = \frac{(z) \cdot (0.005814 + z)}{(0.2035 - z)} = 1.6667 \times 10^{-5}$
 therefore $(z) \cdot (0.005814 + z) = (1.6667 \times 10^{-5}) \cdot (0.2035 - z)$
 therefore $z^2 + z \cdot (0.005814) = (1.6667 \times 10^{-5}) \cdot (0.2035) - z \cdot (1.6667 \times 10^{-5})$
 $\quad \quad \quad = 3.3917 \times 10^{-6} - z \cdot (1.6667 \times 10^{-5})$
 therefore $z^2 + (5.8307 \times 10^{-3}) \cdot z - (3.3917 \times 10^{-6}) = 0$
- Now some of you are not doing 'A' Level Maths and therefore will not know how to solve a quadratic equation so just skip to the answer for "z", but those of you who are doing 'A' Level Maths please do the Maths and see whether I have made any mistakes.
- If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
 and since this will always give **two** answers for "x", then one of them is going to be **in**appropriate in these circumstances. Please do not write down a stupid answer in the exam.
- Here $a = +1.0$
 $b = +(5.8307 \times 10^{-3})$
 $c = -(3.3917 \times 10^{-6})$

$$\text{therefore } z = \frac{-(5.8307 \times 10^{-3}) \pm \sqrt{\{(3.4 \times 10^{-5}) + (1.3567 \times 10^{-5})\}}}{2.0} = \frac{-(5.8307 \times 10^{-3}) \pm (6.897 \times 10^{-3})}{2.0}$$

$$\text{therefore } z = 5.3315 \times 10^{-4}$$

If you had not used a quadratic solution, then your answer would have been about 10% too large. NB You will **not** be asked to use a quadratic equation to solve for “z” in the exams!

- OK, we have found the value for “z”, therefore if we go back to the ICE table on page 19, we will see that $[\text{OH}^-] = (0.005814 + z) = 0.005814 + (5.3315 \times 10^{-4}) = 6.4372 \times 10^{-3}$

$$\text{therefore } \text{pOH} = -\log_{10}(6.4372 \times 10^{-3}) \approx 2.2$$

$$\text{therefore } \text{pH} = 14.0 - 2.2 \approx \mathbf{11.8}$$

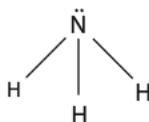
and my guess was right, taking the OH^- ions generated by the CN^- made no difference to the pH value!

- We have added 10 cm^3 of NaOH more than we had at the EP, and to one decimal place **it has made no difference at all**. To find the real difference in the pH value we would have had to use a quadratic solution in each instance and then do everything to five decimal places of working and then round the pH to two or possibly even three places of decimals – and I have no intention of doing that in this exercise. I am doing all this merely to give you an **understanding** of what is going on. I am not concerned about 3/4/5 decimal places in this exercise.
- Now, at this point I want to draw your attention (especially for those of you who want to go into Medicine when you leave school) to something very important about Buffer Solutions. Buffer Solutions consist of a mixture of either
 - i) a **WEAK acid plus a fully dissociated (strong) salt of that Weak Acid**, or
 - ii) a **WEAK base plus a fully dissociated (strong) salt of that Weak Base**
 and their function in Medicine is to protect the organs of the body from rapid changes in pH values (e.g. if by chance you get a drop of acid in your eye/you accidentally inhale some acidic gas/whatever) – and if you now examine the Maths that we have been doing, then you will see that this is exactly what is happening. We added 350 cm^3 of NaOH to the Weak Acid and the resulting pH when we rounded it was **11.8**, and then when we added another 10 cm^3 of NaOH to this particular Buffer Solution, when we rounded it **the pH was still 11.8** – but there would have been an increase in the pH value if we had calculated the pH to the third or fourth decimal place⁴.
- **That is what a Buffer Solution is all about. It is meant to buffer / to absorb the shock of the addition of a small amount of either an acid or a base without any significant change in the pH value – and our calculations show that this is indeed what has happened here!**
- OK, I have now taken you through the calculations that you need to make in order to track the changes that take place in the pH values when you titrate
 - Section A) a Strong Acid against a Strong Base, and
 - Section B) a Weak Acid against a Strong Base.
- What about a Weak Acid against a Weak Base?
Well, let us try that.

⁴ In any case, you ought to keep in mind that burettes and pipettes are made to an accuracy of about $\pm 0.05 \text{ cm}^3$, so if you start doing your calculations to too many places of decimals, then you are deceiving yourself with spurious and unjustified accuracy.

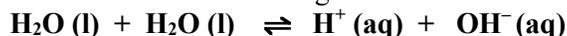
Section C: an analysis of the Maths for Weak Bases/Strong Acids

- In Section B we looked at the titration of a Weak Acid (HCN) against a Strong Base (NaOH), so before you do anything, I would like you to close your eyes and just think through what ought to be done for a Strong Acid against a Weak Base. The sort of things that you should consider are
 - when should I use an ICE table?
 - which bits of “z” can I safely ignore because they will affect my ultimate pH value hardly at all?
 - which half of the S-shaped curve am I in: am I in the base part of the curve or in the acid part of the curve, and therefore am I calculating the pH straight away, or do I have to start by calculating the pOH value?
 - have I understood the usage of the Henderson-Hasselbalch equation in this procedure, and where will it fit in here?
- When you are satisfied that you have answered all those questions, then could you start reading.
- Let us start by understanding what a Weak Base is. It is a base that reaches dynamic equilibrium when it has dissociated only a tiny proportion of its ions. **OK, but what exactly is NH₃ dissociating?**
- Now let us get this very clear. If it were dissociating one of its H⁺ ions then it would be an **ACID**. **Therefore it is not dissociating an H⁺ ion!**

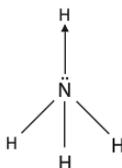


This is all that NH₃ consists of!

- Is it dissociating its N atom? **NO, it is not.** I do not want to get into abstruse theoretical Chemistry, but just take my word for it. **The three H atoms do not throw the N atom overboard.** In a sense therefore the verb “dissociating” is a misnomer. **NH₃ does not dissociate anything at all!** What is happening is that it is pure Water that is “dissociating” in the reaction of NH₃ dissolving in Water.



and it is then the H⁺ ion from the dissociation of pure Water that latches onto the lone pair of electrons in the NH₃ via a dative bond



and thus when it is said that NH₃ is a Weak Base, this is what is meant



- NH₃ is a Brønsted-Lowry **base** because it is **proton acceptor**, and it is the fact that Water dissociates hardly any protons that causes the dynamic equilibrium to lie so far to the left and thus makes NH₃ a “weak” base.
- Isn't that lovely. All that we have done is use our brains and we have understood something that lightly tripped off the pen of a learned Prof who learnt his/her Chemistry long long ago, and has forgotten that we poor Chemistry students have not a clue as to what on earth he/she is talking about.

- OK, here, we are going to titrate 100 cm³ of 0.50 mol dm⁻³ (i.e. 0.05 mol) of NH₃ (a Weak Base) against
 - 100 cm³ of 0.25 mol dm⁻³ (i.e. 0.025 mol) of the strong acid HCl
 - 200 cm³ of 0.25 mol dm⁻³ (i.e. 0.050 mol) of the strong acid HCl ← **This is the Equivalence Point.**
 - 201 cm³ of 0.25 mol dm⁻³ (i.e. 0.05025 mol) of the strong acid HCl
 - 225 cm³ of 0.25 mol dm⁻³ (i.e. 0.05625 mol) of the strong acid HCl, and
K_b for NH₃ is 1.778 x 10⁻⁵, and K_a · K_b = 1 x 10⁻¹⁴ therefore K_a would be 5.623 x 10⁻¹⁰.
- From what I stated in blue above, you can rightly infer that I have put 100 cm³ of 0.50 mol dm⁻³ NH₃ (a Weak Base) in a conical flask (in real life you would use only say 25 cm³, but we are doing this for the Maths and not as a lab experiment), and into this I am going to titrate the successive amounts of HCl (aq).

NH₃ is a Weak Base, therefore to calculate the pH value of the NH₃ before adding any HCl, we must use an ICE table

Concentration	[NH ₃]	[H ₂ O]	⇌	[NH ₄ ⁺]	[OH ⁻]
I (for Initial)	0.5	1.0		0	0
C (for Change)	-z	ignore		+z	+z
E (for at Equilibrium)	(0.5-z)	1.0		z	z

- NH₃ is a base therefore we are dealing with K_b instead of K_a, and

$$K_b = \frac{z \cdot z}{(0.5-z)} = 1.7783 \times 10^{-5} \text{ therefore } z^2 = (1.7783 \times 10^{-5}) \times (0.5-z)$$

but $z \cdot (1.7783 \times 10^{-5})$ is going to be so small as to not affect the value of the pH to one decimal place therefore we can (as we did in Section B) ignore it and just solve for $z^2 = (1.7783 \times 10^{-5}) \times (0.5)$
therefore $z = 2.9819 \times 10^{-3}$, therefore $\text{pOH} = -\log_{10}(2.9819 \times 10^{-3}) \approx 2.53$
therefore $\text{pH} = 14.0 - 2.53 \approx 11.5$.

- That is the pH of the Ammonia at the start before any HCl is added to it.
- On page 20 I asked you to think about
 - when should I use an ICE table?
 - which bits of “z” can I safely ignore because they will affect my ultimate pH value hardly at all?
 - which half of the S-shaped curve am I in: am I in the base part of the curve or in the acid part of the curve, and therefore am I calculating the pH straight away, or do I have to start by calculating the pOH value?
- Well, I hope that you got all of that right.
- The next thing that I asked you to think about was
 - have I really understood the usage of the Henderson-Hasselbalch equation in this procedure, and where will it fit in here?

and we will now see whether you allowed for that correctly.

Section Ca) The pH value after adding 100 cm³ of 0.25 mol dm⁻³ HCl (that takes me to the EP)

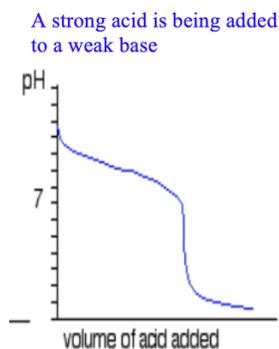
- N of NH₃ = C x V in dm³ = 0.50 mol dm⁻³ x 100 cm³ = 0.50 mol ~~dm⁻³~~ x 0.100 ~~dm³~~ = 0.05 mol.
N of HCl = C x V in dm³ = 0.250 mol ~~dm⁻³~~ x 0.100 ~~dm³~~ = 0.0250 mol.
There is now 0.025 mol of NH₃ **un-neutralised**.

- The reaction equation is
$$\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$$

The Mole Reaction Ratio is
$$\begin{array}{cccc} 1 & 1 & 1 & 1 \end{array}$$

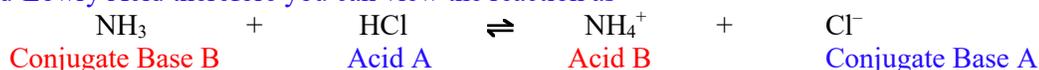
therefore 0.025 mol of HCl will react with 0.025 mol of NH₃ and leave **0.025 mol of NH₃ unreacted** and since the Mole Reaction Ratio is 1 : 1 : 1: 1, **0.025 mol of NH₄⁺** will have been formed.

- If you add 100 cm³ of HCl to 100 cm³ of NH₃, then the volume is now 200 cm³ of total solution (in the conical flask), and in terms of concentrations you have 0.025 mol of NH₄⁺ ÷ (200 ÷ 1000) dm³ = 0.125 mol dm⁻³ of NH₄⁺ (aq) Ammonium, and exactly the same concentration i.e. 0.125 mol dm⁻³ of unreacted NH₃ (aq) – and these are the concentrations that we will have to use in an ICE table.
- One of the questions that I asked you to ask yourself was “which half of the S-shaped curve am I in?”, and the answer to that question is that in Section (Ca) we are in the top half of this particular curve (below) where the Weak Base NH₃ is gradually being neutralised by the strong acid HCl.



Source: chemguide

- Mr Clark has drawn his curve too steeply. The Buffer Solution parts of the curve should have been drawn much flatter (and we have demonstrated mathematically that in the buffering part of the curve the pH changes hardly at all).
- One of the other questions that I asked you to ask yourself was “have I really understood the usage of the Henderson-Hasselbalch equation in this procedure, and where will it fit in here?”, and I hope that you will have said to yourself “A Weak Base plus a fully dissociated (strong) salt of that Weak Base will give me a Buffer Solution, and equally a buffer solution will exist where the concentrations of an acid and its conjugate base are approximately equal (and it will certainly exist when they are equal)”.
- You will therefore have guessed correctly that you will need to use the Henderson-Hasselbalch equation in Section (Ca) and, as you will see, you will need it because the concentrations of both Ammonium and Ammonia are = 0.125 mol dm⁻³, and **anything that dissociates a proton is a Brønsted-Lowry Acid therefore you can view the reaction as**



NB The reaction of Cl⁻ with Water is so small that we can ignore the effect on the pH of Cl⁻.

- We know that K_b for Ammonia is 1.7783×10^{-5} (therefore K_a would be 5.6233×10^{-10}), therefore let us now fill in our Henderson-Hasselbalch equation, but please remember that when $[A^-] = [HA]$ then the ratio of the two = 1 , and the $\log_{10}(1) = 0$, therefore

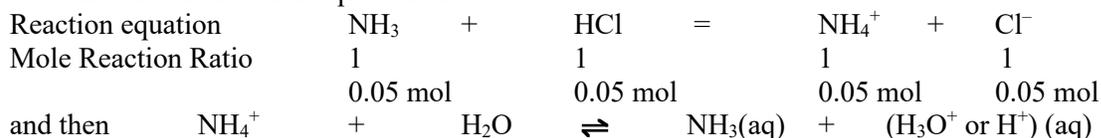
$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \left\{ \frac{[A^- (\text{aq})]}{[HA (\text{aq})]} \right\} \frac{\text{Concentration of the SALT}}{\text{Concentration of the ACID}} \\ &= -\log_{10}(5.6233 \times 10^{-10}) = \mathbf{9.25} . \end{aligned}$$

- We started with a solution in the conical flask (NH_3) that had a pH of **11.5**, and then when we added 100 cm^3 of $0.25 \text{ mol dm}^{-3} \text{ HCl}$ the pH dropped to **9.25**.
- What is going to happen when we add 200 cm^3 to the Ammonia.

Section Cb) The pH value after adding 200 cm^3 of $0.25 \text{ mol dm}^{-3} \text{ HCl}$

- We are now adding 0.05 mol of HCl to 0.05 mol of NH_3 , therefore we are at the Equivalence Point. However, just as in Section B, I reminded you that for
 - a **Strong Acid** with a **Strong Base**, the Equivalence Point will always be at **7.0** at 298K
 - a **Strong Acid** with a Weak Base, the Equivalence Point **will always be < 7.0** at 298K
 - a Weak Acid with a **Strong Base**, the Equivalence Point **will always be > 7.0** at 298K
 so let us start doing our calculations – and please go back and look at the titration curve on page 22 and you will see that we are now in the bottom part of the curve so if the pH value that we calculate is not less than **7.0** then we have done something wrong! (That is the lovely thing about Chemistry. When everything starts to fall into place, then you often have signposts to tell you whether or not you are on the right road.)

- We can write the reaction equation as



- In other words, the Ammonium and the Water, through a reversible reaction, **are constantly generating Ammonia and H^+ ions**, and at the position of dynamic equilibrium, in order to calculate the pH value, we must therefore create an ICE table and use the Henderson-Hasselbalch equation.
- After adding 200 cm^3 of acid to 100 cm^3 of Ammonia we will have $V = 300 \text{ cm}^3$ in total of the solution in our conical flask, therefore the Concentration of NH_4^+ will (from the above Mole Reaction Ratio) be given by $C = N \div V$ in $\text{dm}^3 = 0.05 \text{ mol} \div (300 \div 1000) \text{ dm}^3 = 0.166667 \text{ mol dm}^{-3}$

- From the reversible reaction, our ICE table is

Concentrations	$[\text{NH}_4^+]$	$[\text{H}_2\text{O}]$	$[\text{NH}_3]$	$[\text{H}^+]$
I for Initial	0.167	1.0	0	0
C for Change	-z	ignore	z	z
E for at Equilibrium	$(0.167-z)$	1.0	z	z

$$\text{therefore } K_a = 5.6233 \times 10^{-10} = \frac{z \cdot z}{(0.167-z)}$$

$$\text{therefore } z^2 = (5.6233 \times 10^{-10}) \times (0.167-z)$$

$$\text{therefore } z^2 = (9.3722 \times 10^{-11}) - (5.6233 \times 10^{-10}) \cdot z$$

and we can ignore the bit in red because using a quadratic solution will not affect the pH value that will be given to one decimal place

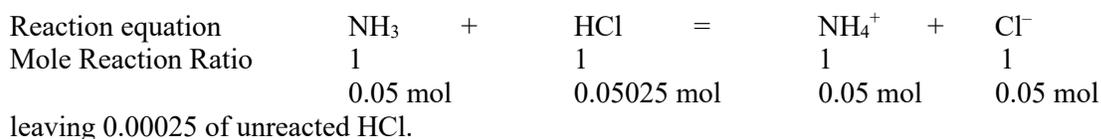
$$\text{therefore } z^2 = 9.3722 \times 10^{-11} \quad \text{and } z = 9.681 \times 10^{-6}$$

$$\text{and } \text{pH} = -\log_{10}(9.681 \times 10^{-6}) \approx \mathbf{5.0}$$

- We know that for the titration of a Strong Acid against a Weak Base, at the Equivalence Point the pH of the solution will be less than 7.0, and indeed our answer is less than 7.0. (I may well have made a mistake in pressing the wrong buttons on my calculator, but at least I know that my answer is in the right ball park.)
- We started with a solution in the conical flask (NH_3)
 - that had a pH of **11.5**, and then
 - when we added 100 cm^3 of 0.25 mol dm^{-3} HCl the pH dropped to **9.25**, and then
 - when we added 200 cm^3 of 0.25 mol dm^{-3} HCl, at the EP, the pH has dropped to **5.1** .
- What then would happen if we were to add 201 cm^3 of the HCl?

Section Cc) The pH on adding 201 cm^3 of 0.25 mol dm^{-3} (i.e. 0.05025 mol) of the strong acid HCl

- You now know enough of the explanations for me to just get on and do the calculations.
- We started with 0.05 mol of NH_3 and we have added 0.05025 mol of HCl to it, therefore we neutralised all the NH_3 and there are now 0.00025 mol of unreacted HCl in the solution.
- We started with 100 cm^3 of NH_3 and we have added 201 cm^3 of HCl to it, therefore the volume of the total solution = 301 cm^3 .
- The concentration of the HCl is thus now $8.30565 \times 10^{-4} = [\text{H}^+] = 0.0008306$.
- Therefore $\text{pH} = -\log_{10}(8.30565 \times 10^{-4}) \approx \mathbf{3.1}$.
- However, at this point **I have taken into account merely the concentration of the Strong Acid HCl**. I have not taken into account the Weak Acid that was produced by the reaction of Ammonia and the Strong Acid. Let me therefore now take this into account and see whether that affects the value of the pH .



- The concentration of NH₄⁺ = 0.05 mol ÷ (301 ÷ 1000) dm³ = 0.166113 mol dm⁻³.
- I can now create an ICE table where [H⁺] from the Strong Acid = 0.0008306 mol dm⁻³ from page 26, and [NH₄⁺] = 0.166113 mol dm⁻³ from above.

Concentrations	[NH ₄ ⁺]	[H ₂ O]	[NH ₃]	[H ⁺]
I for Initial	0.166113	1.0	0	0.0008306
C for Change	-z	ignore	z	z
E for at Equilibrium	(0.166113-z)	1.0	z	(0.0008306 + z)

$$\text{therefore } K_a = 5.6233 \times 10^{-10} = \frac{z \cdot (0.0008306 + z)}{(0.166113 - z)}$$

$$\text{therefore } (5.6233 \times 10^{-10}) \times (0.166113 - z) = z \cdot (0.0008306 + z)$$

$$\text{therefore } z^2 = (9.341 \times 10^{-11}) - (5.6233 \times 10^{-10}) \cdot z = z \cdot (0.0008306) + z^2$$

and we can ignore the bits in red because using a quadratic solution will not affect a pH value given to one decimal place

$$\text{therefore } z^2 = 9.341 \times 10^{-11} \text{ and } z = 9.665 \times 10^{-6}$$

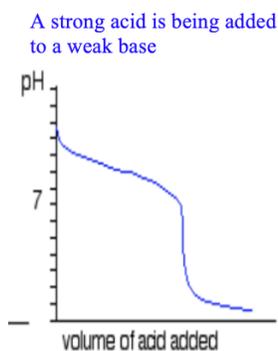
$$\text{therefore } [\text{H}^+] = (0.0008306 + z) = 8.4026 \times 10^{-4} \text{ and } -\log_{10}(8.4026 \times 10^{-4}) \approx 3.07$$

therefore the pH of the solution when you take into account the H⁺ ions released by BOTH the HCl and the NH₄⁺ is still **3.1** to one decimal place (which is how pH values are most often given).

- In other words taking into account the release of H⁺ ions when NH₄⁺ reacts with Water did not make any difference to the pH value as it is normally expressed. It was the H⁺ ions released by the HCl that determined the pH value of the resulting solution **even though we added literally just 1 cm³ ONE TINY CUBIC CENTIMETRE of HCl more than the volume of HCl at the Equivalence Point.**
- Let us now find out what would happen to the pH if we added 225 cm³ to the 100 cm³ of NH₃?

Section Cd) The pH on adding 225 cm³ of 0.25 mol dm⁻³ (i.e. 0.05625 mol) of the strong acid HCl

- We are adding 0.05625 mol of the strong acid HCl.
There were 0.05 mol of the weak Base NH₃.
Therefore we are left with 0.00625 of unreacted HCl in 325 cm³ of total solution.
- $C = N \div V$ in dm³, therefore $[H^+] = 0.00625 \text{ mol} \div (325 \div 1000) \text{ dm}^3 = 0.019231 \text{ mol dm}^{-3} = [H^+]$.
- $\text{pH} = -\log_{10}(0.019231) \approx 1.7$.
- This bit of the calculation is ridiculously easy because we do not have to worry about the effect of the NH₄⁺ because as we saw in the last Section the effect is overwhelmed by the effect of the H⁺ ions that are dissociated by the HCl.
- We can now make one last check to see whether our numbers are in the right ballpark. We started with an acid with a concentration of 0.025 mol dm⁻³ and after neutralising the NH₃, the finishing total solution in the flask had a concentration of 0.019 of H⁺ ions. In other words the finishing concentration was just less than the initial un-neutralised concentration, and we got a titration curve which resembled the classic Strong Acid vs Weak Base curve.



Source: chemguide

- **I don't know about you, but I loved doing all the Maths in this note. I LOVE using my brain, and I hope that you also love your brain. When you came to me almost two years ago, I said that I wanted you to fall in love with your brains because, sadly even though relationships/friendships in life break down, your relationship with your brain will never let you down. If you look after it, your brain will be the best friend that you have during the whole of your life!**⁵

⁵ I was unbelievably lucky in that I met a girl on the third day of our very first term at University, and I fell in love with her on the spot/there and then, and four days later I asked her to marry me, and 50 deliriously/gloriously happy years later she died of cancer. **She was the loveliest human being whom I met in the whole of my life.** She was a really nice girl ■.