ACIDS & BASES

ACID-BASE TITRATIONS (NOTES)

CHEMISTRY 165 // SPRING 2020

DR. MIOY T. HUYNH | 2020

Inventory of what we've covered so far

We have considered acids and bases separately:

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq) \qquad BOH\ (aq) \rightleftharpoons B^+\ (aq) + OH^-\ (aq)$$

We have considered mixing acids and bases together:

$$\underbrace{HA}_{\textbf{acid}}\ (aq) + \underbrace{BOH}_{\textbf{base}}\ (aq) \rightleftharpoons \underbrace{H_2O}_{\textbf{water}}\ (l) + \underbrace{BA}_{\textbf{salt}}\ (aq)$$

We have considered how aqueous salts (BA) can be acidic, basic, or neutral in water.

We have considered the mixture of weak acids/bases with salts to form buffers.

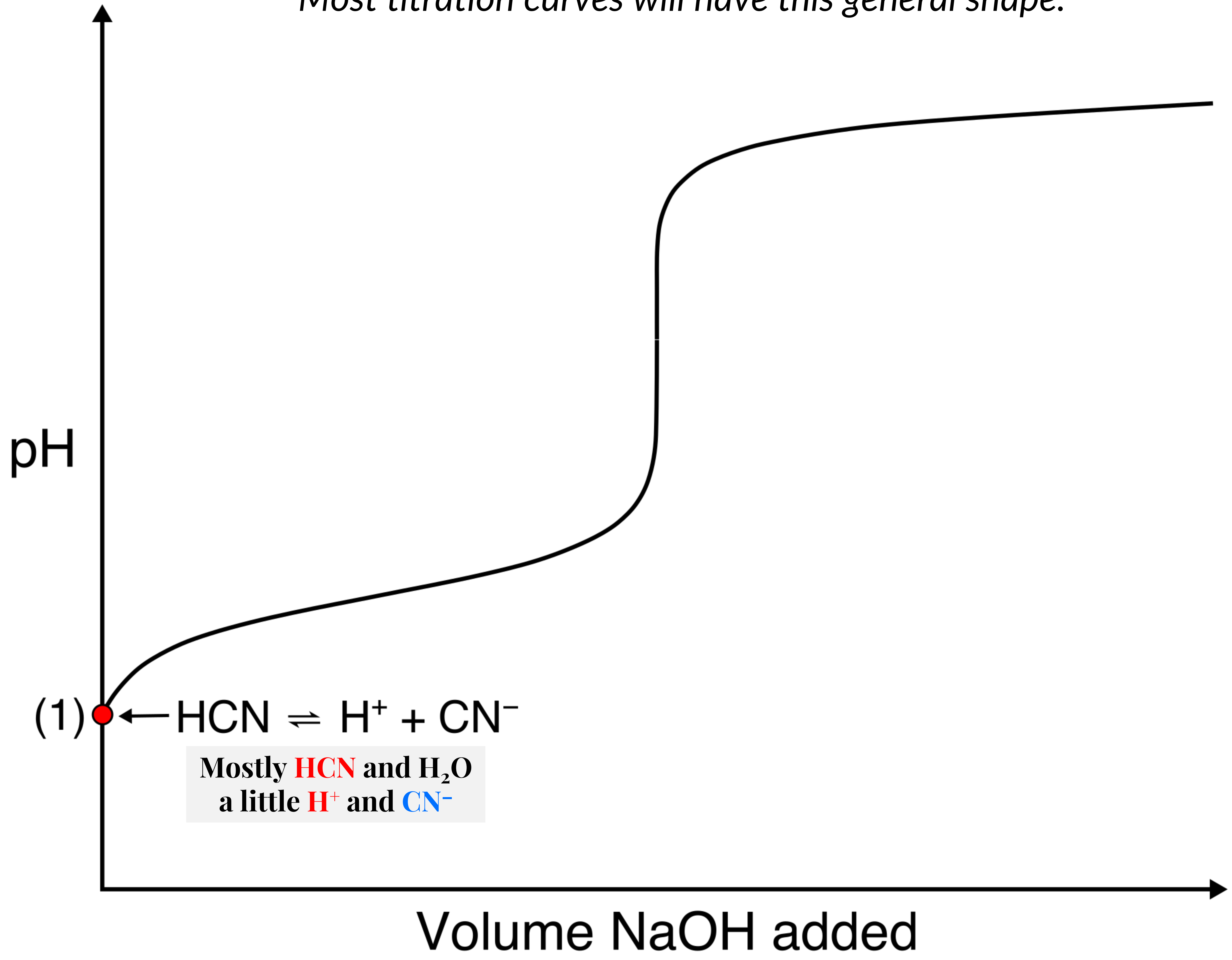
Now we will look into mixing acids and bases together more closely, through what we call acid-base titrations; namely, we are interested in how our pH changes as titrant is added to an acidic or basic solution.

You will find that titrations combine all of the concepts we've already discussed, so nothing "new" will pop up.

Titration curves

Titrating a weak acid (HCN) with a strong base (NaOH → Na^{+} + OH^{-}).

Most titration curves will have this general shape.



<u>What's happening at point (1)?</u>

We haven't added any base yet. At this point, we have just our weak acid (HCN).

What will the solution do at this point?

Well, HCN will dissociate a little (it's a weak acid) and reach equilibrium. So, set up an ICE chart:

	acid				conjugate-base
	HCN	⇌	H^{+}	+	CN^{-}
I	$[HCN]_0$		0		0
C	– x		+ x		+ x
E	$[HCN]_0$ – x		x		x

Then, we can set up an expression for K_a to find pH.

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = \frac{x^2}{[HCN]_0 - x} \rightarrow x = [H^+] \rightarrow pH$$

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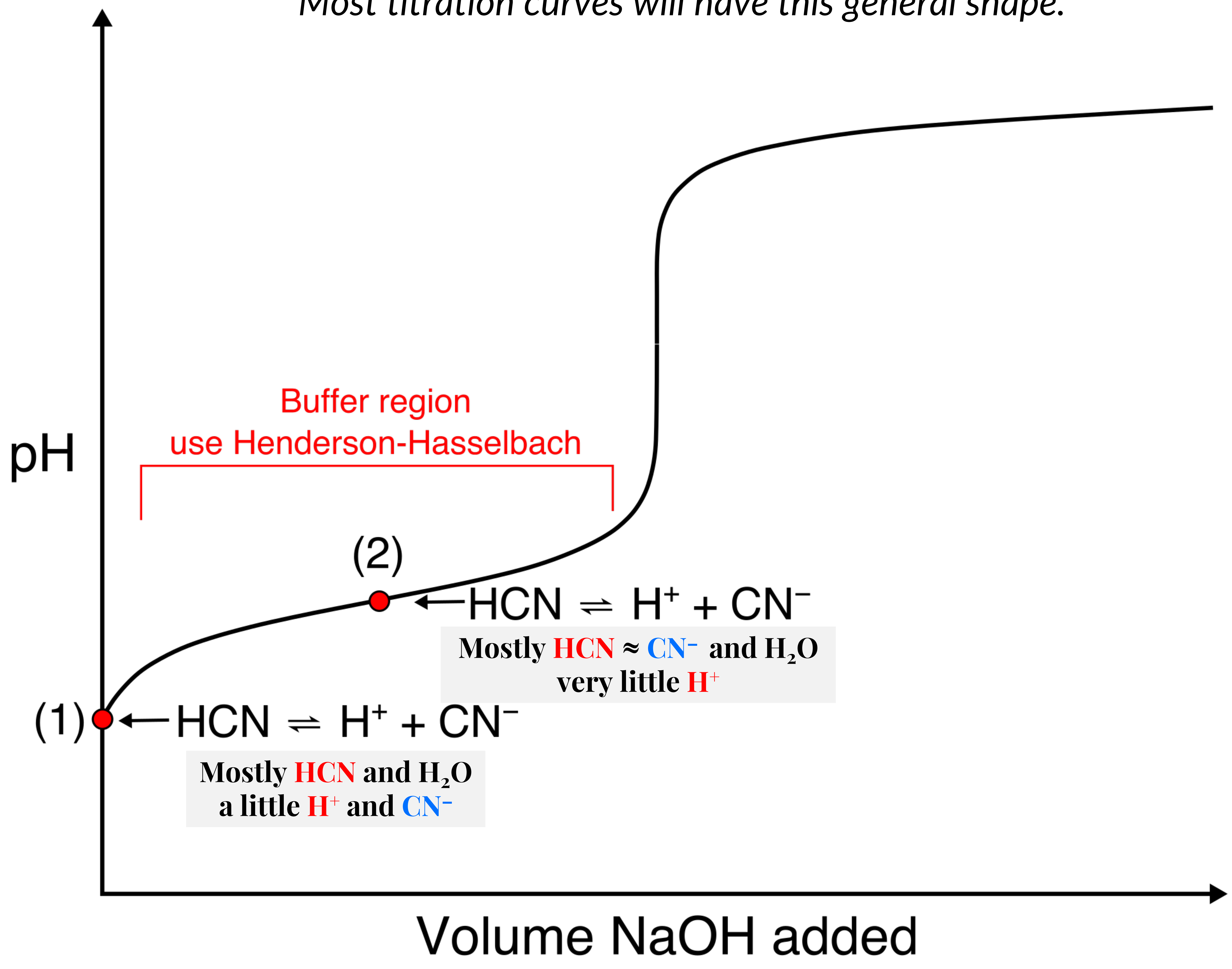

What's happening at point (2)?

We are now adding base. So we need to first consider the reaction between HCN and OH^-:

$$HCN + Na^+ + OH^- \rightarrow H_2O + Na^+ + CN^-$$

	acid				conjugate-base
	HCN	+	OH^-	→	CN^-
I	n_{HCN}		n_{OH}		0
C	$-\ n_{OH}$		$-\ n_{OH}$		$+\ n_{OH}$
F	$n_{HCN} - n_{OH}$		0		n_{OH}

Next, we need to consider the process of these new concentrations to reach equilibrium. But we can take a shortcut because we see that there is both HCN and CN^- in solution: it's a buffer!

So we can apply Henderson-Hasselbalch to find pH:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{CN}^-]}{[\mathrm{HCN}]}$$

Titration curves

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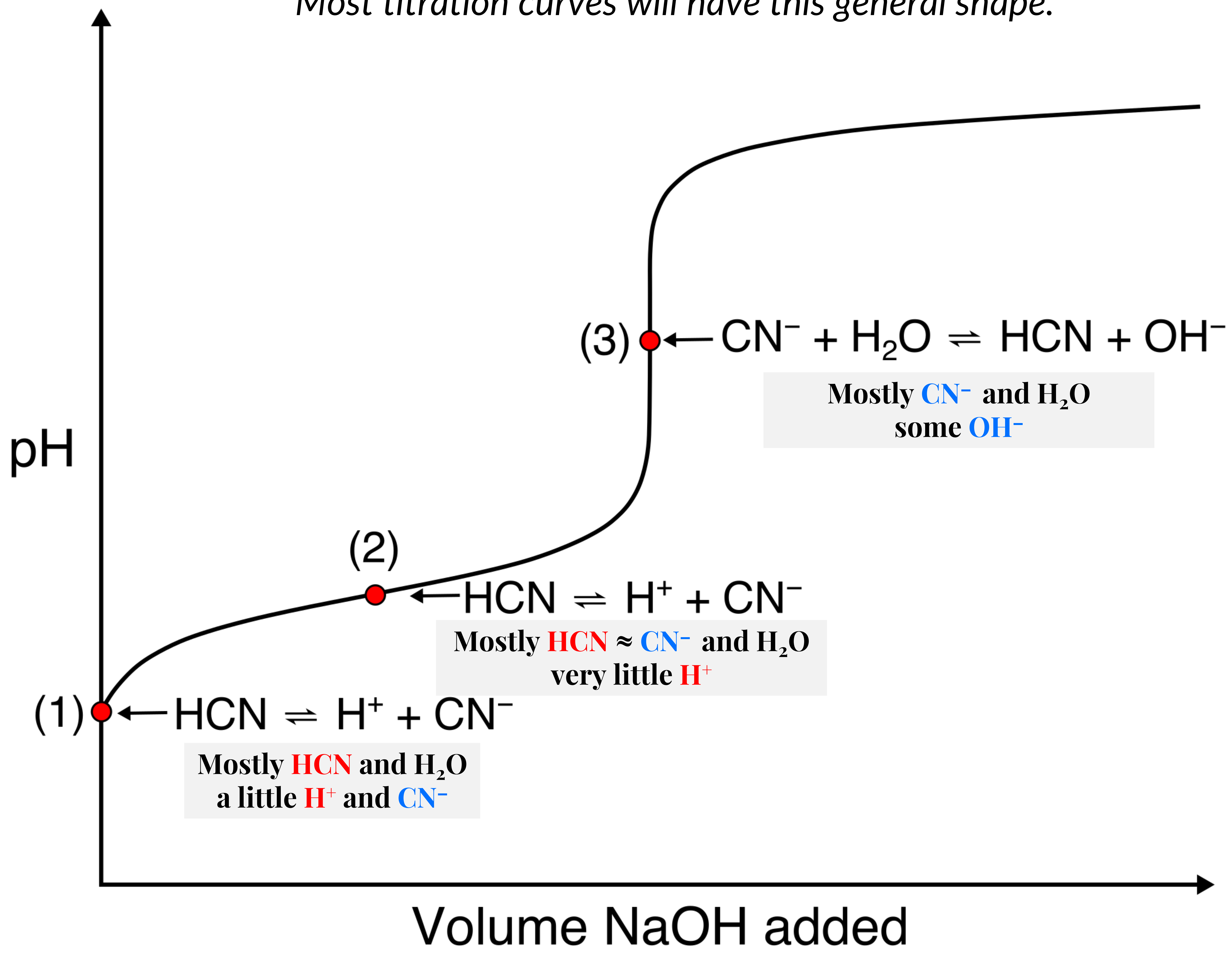

<u>What's happening at point (3)?</u>

We are at the equivalence point where $n_{HCN} = n_{OH}$. Again, we need to consider the reaction between HCN and OH^- but both react completely now!

$$HCN + Na^+ + OH^- \rightarrow H_2O + Na^+ + CN^-$$

	HCN	+	OH^-	→	CN^-
I	n_{HCN}		n_{OH}		0
C	$-\ n_{OH}$		$-\ n_{OH}$		$+\ n_{OH}$
F	0		0		n_{OH}

Now what? Well, CN^- is a (conjugate-)base, so it will accept a H^+ from water via:

	CN^-	+	H_2O	⇌	HCN	+	OH^-
I	$[CN^-]$		--		0		0
C	$-\ x$		--		$+\ x$		$+\ x$
E	$[CN^-] - x$		--		x		x

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} = \frac{x^2}{[CN^-] - x} \rightarrow x = [OH^-] \rightarrow pH$$

Titration curves

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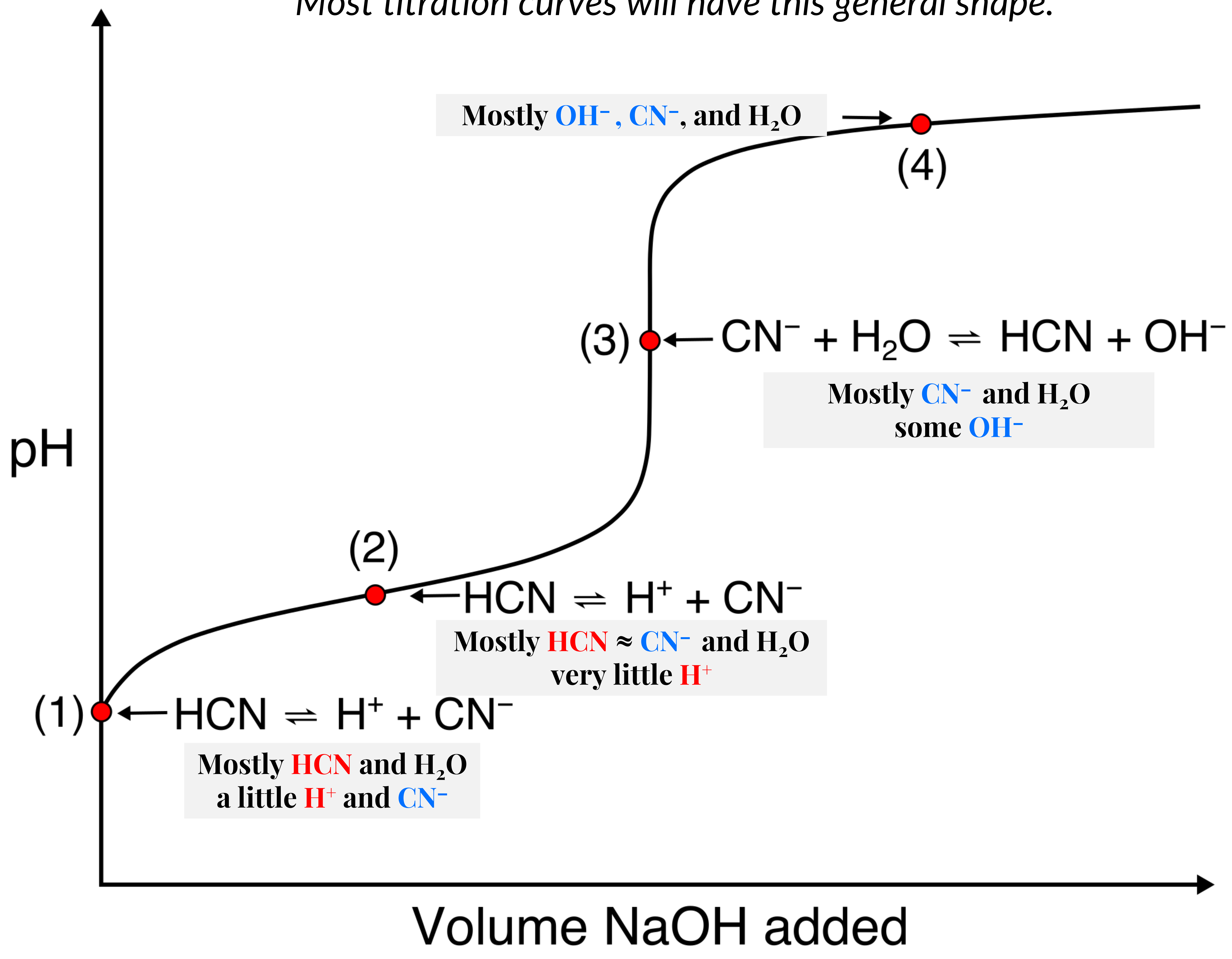
Most titration curves will have this general shape.



What's happening at point (4)?

We are past the equivalence point and are now adding *excess* OH^-. Again, we need to consider the reaction between HCN and OH^- but HCN will be limiting now!

$$HCN + Na^+ + OH^- \rightarrow H_2O + Na^+ + CN^-$$

	HCN	+	OH^-	→	CN^-
I	n_{HCN}		n_{OH}		0
C	$-\ n_{HCN}$		$-\ n_{HCN}$		$+\ n_{HCN}$
"E"	0		$n_{OH} - n_{HCN}$		n_{HCN}

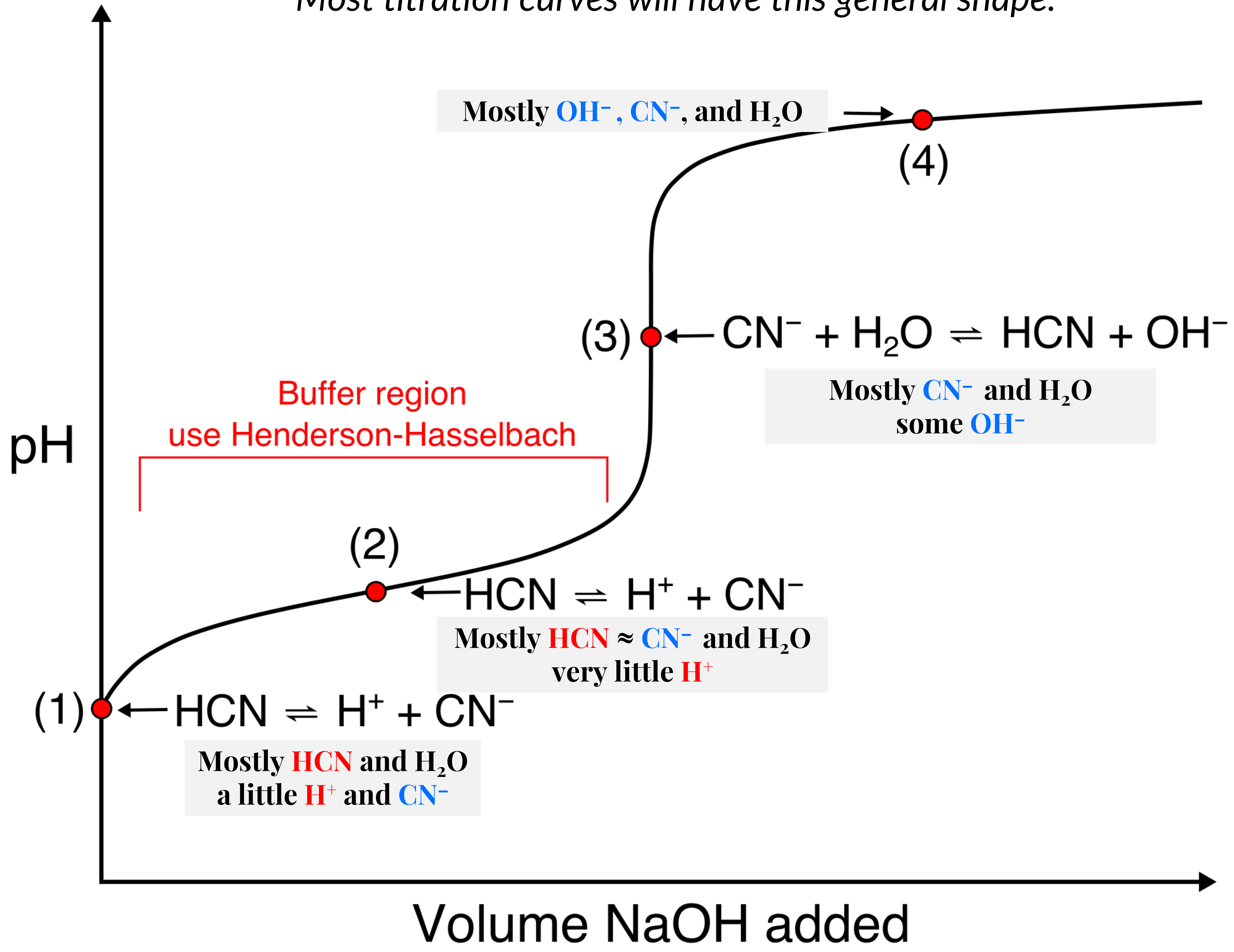
Because OH^- is a stronger base than CN^-, we need only consider its effect on pH:

$$pOH = -\log[OH^-] \rightarrow pH = 14 - pOH$$

Titration curves

Titrating a weak acid (HCN) with a strong base ($NaOH \rightarrow Na^+ + OH^-$).

Most titration curves will have this general shape.



RECAP

At point (1): We haven't added any NaOH, so the pH comes from the weak acid equilibrium.

At point (2): This is called the midpoint because we have added exactly half of what we need to get to the equivalence point.

Here [HCN] = [CN^-] and pH = pK_a.

Near point (2): This region is the buffer region, where we have HCN and CN^- in solution, so you can apply the Henderson-Hasselbalch equation to get pH.

At point (3): You add exactly $n_{HCN} = n_{OH}$ and make the salt NaCN. Here you only have the conjugate-base (CN^-) reacting with water, which will determine the pH.

After point (3): You are adding *excess* OH, which will completely determine the pH.