



ACIDS & BASES

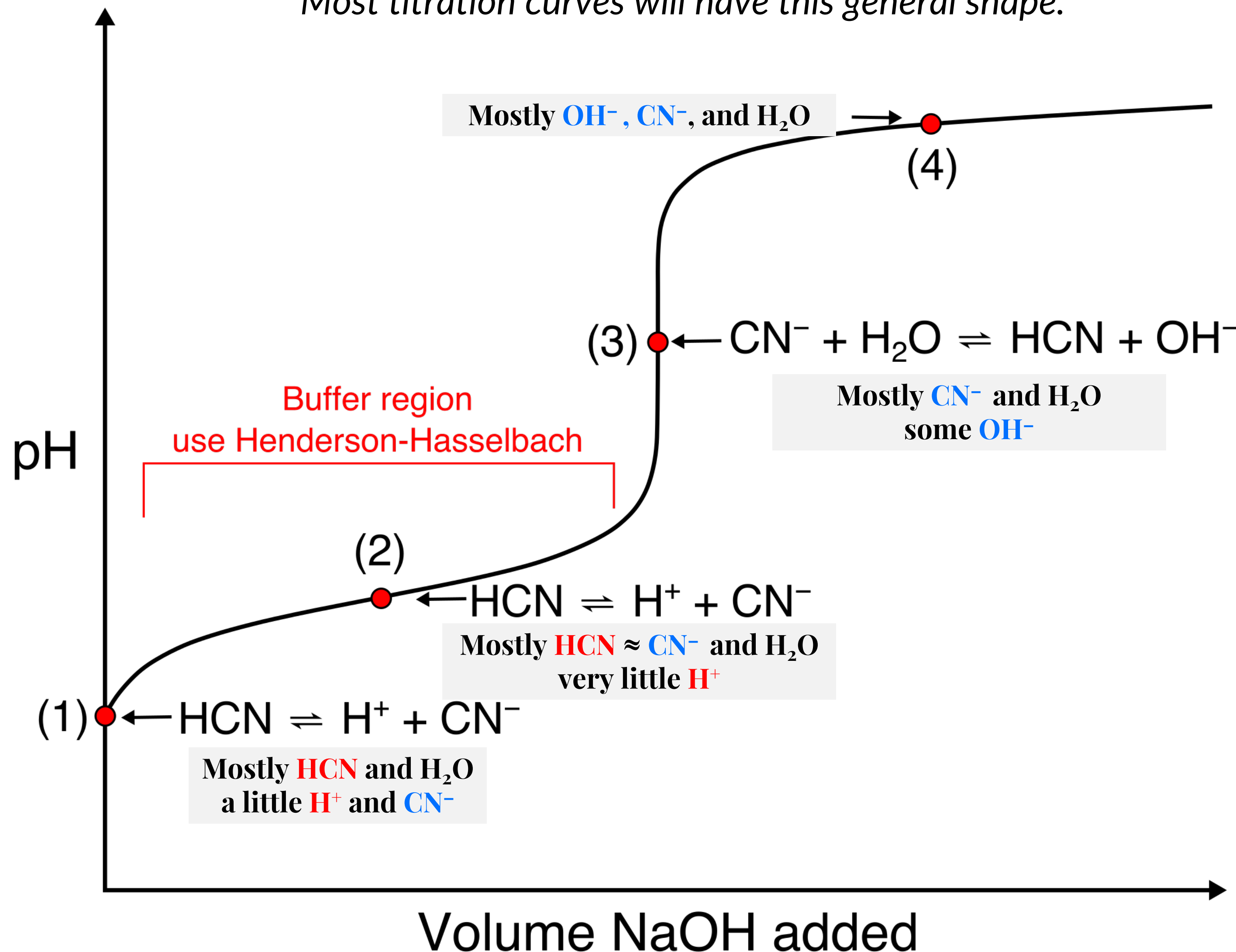
ACID-BASE TITRATIONS (PROBLEMS)

CHEMISTRY 165 // SPRING 2020

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 $\text{pH} = \text{pK}_a$.

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 $n_{\text{HCN}} = n_{\text{OH}}$ 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.

PRACTICE PROBLEM 1

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution initially, before any NaOH is added.

— *answer* —

PRACTICE PROBLEM 1

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution initially, before any NaOH is added.

— answer —

At this point, we have only the weak acid dissociating in water since no NaOH has been added.

Thus, we can set up the weak acid dissociation equilibrium in water.

We can construct an ICE chart for this equilibrium, set up a K_a expression, solve for x , and determine the pH.

	HNO_2	\rightleftharpoons	H^+	+	NO_2^-
I	0.50 M		0 M		0 M
C	- x		+ x		+ x
E	0.50 - x		x		x

Because the value of K_a is very small, we know that the system will undergo very little change (x value) toward the right in order to achieve equilibrium. In other words, we can take “ x ” to be very small/negligible and invoke the approximation that:

$$0.50 - x \approx 0.50$$

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.0 \times 10^{-4}$$

$$4.0 \times 10^{-4} = \frac{(x)(x)}{0.50 - x}$$

$$4.0 \times 10^{-4} \approx \frac{x^2}{0.50}$$

$$x = 0.0014_1 \text{ M} = [\text{H}^+]$$

$$\text{pH} = -\log(0.0013_3) = 1.85$$

PRACTICE PROBLEM 2

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 250. mL of 0.50 M NaOH are added.

— *answer* —

PRACTICE PROBLEM 2

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 250. mL of 0.50 M NaOH are added.

— answer —

At this point, we have added some NaOH, which is a strong base, so remember: $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

First, determine how much OH^- we have added:

$$n_{\text{HNO}_2} = 1.0 \text{ L} \times \frac{0.50 \text{ mol HNO}_2}{1 \text{ L}} = 0.50 \text{ mol HNO}_2 \quad n_{\text{OH}^-} = 0.250 \text{ L} \times \frac{0.50 \text{ mol OH}^-}{1 \text{ L}} = 0.125 \text{ mol OH}^-$$

So we are not at the equivalence point and can use the Henderson-Hasselbalch equation to find the pH.

Second, we need to consider the reaction between HNO_2 and OH^- using an ICF chart:

	HNO_2	+	OH^-	\rightarrow	NO_2^-	+	H_2O
I	0.50 mol		0.125 mol		0 mol		n/a
C	- 0.125		- 0.125		+ 0.125		n/a
F	0.375		0		0.125		n/a
	\rightarrow 0.300 M		0 M		0.100 M		n/a

Convert to M
by dividing by
 $V_{\text{tot}} = 1.25 \text{ L}$

Use the Henderson-Hasselbalch equation to find pH.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \\ &= -\log(4.0 \times 10^{-4}) + \log \frac{[0.10_0]}{[0.30_0]} \\ &= 3.39_8 - 0.47_7 \\ \text{pH} &= 2.92 \end{aligned}$$

PRACTICE PROBLEM 3

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 500. mL of 0.50 M NaOH are added.

— *answer* —

PRACTICE PROBLEM 3

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 500. mL of 0.50 M NaOH are added.

— answer —

At this point, we have added some NaOH, which is a strong base, so remember: $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

First, determine how much OH^- we have added:

$$n_{\text{HNO}_2} = 1.0 \text{ L} \times \frac{0.50 \text{ mol HNO}_2}{1 \text{ L}} = 0.50 \text{ mol HNO}_2 \quad n_{\text{OH}^-} = 0.500 \text{ L} \times \frac{0.50 \text{ mol OH}^-}{1 \text{ L}} = 0.25 \text{ mol OH}^-$$

So we are not at the equivalence point and can use the Henderson-Hasselbalch equation to find the pH.

Second, we need to consider the reaction between HNO_2 and OH^- using an ICF chart:

	HNO_2	+	OH^-	\rightarrow	NO_2^-	+	H_2O
I	0.50 mol		0.25 mol		0 mol		n/a
C	- 0.25		- 0.25		+ 0.25		n/a
F	0.25		0		0.25		n/a
	\rightarrow 0.17 M		0 M		0.17 M		n/a

Convert to M
by dividing by
 $V_{\text{tot}} = 1.50 \text{ L}$

Use the Henderson-Hasselbalch equation to find pH.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \\ &= -\log(4.0 \times 10^{-4}) + \log \frac{[0.17]}{[0.17]} \\ &= 3.39_8 + 0 \\ \text{pH} &= 3.40 \end{aligned}$$

This is the midpoint where $[\text{HNO}_2] = [\text{NO}_2^-]$ and

$$n_{\text{OH}^-} = \frac{1}{2} \times n_{\text{HNO}_2}$$

PRACTICE PROBLEM 4

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 1000. mL of 0.50 M NaOH are added.

— *answer* —

PRACTICE PROBLEM 4

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 1000. mL of 0.50 M NaOH are added.

— answer —

At this point, we have added some NaOH, which is a strong base, so remember: $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

First, determine how much OH^- we have added:

$$n_{\text{HNO}_2} = 1.0 \text{ L} \times \frac{0.50 \text{ mol HNO}_2}{1 \text{ L}} = 0.50 \text{ mol HNO}_2 \quad n_{\text{OH}^-} = 1.000 \text{ L} \times \frac{0.50 \text{ mol OH}^-}{1 \text{ L}} = 0.50 \text{ mol OH}^-$$

We are at the equivalence point. Second, we need to consider the reaction between HNO_2 and OH^- using an ICF chart:

$n_{\text{OH}^-} = n_{\text{HNO}_2}$		HNO_2	+	OH^-	\rightarrow	NO_2^-	+	H_2O	
	I	0.50 mol		0.50 mol		0 mol		n/a	
	C	-0.50		-0.50		+0.50		n/a	
	F	0		0		0.50		n/a	
Convert to M by dividing by $V_{\text{tot}} = 2.00 \text{ L}$		0 M		0 M		0.25 M		n/a	

Now we consider the weak-base (NO_2^-) equilibrium:

	NO_2^-	+	H_2O	\rightleftharpoons	HNO_2	+	OH^-	
I	0.25 M		n/a		0 M		0 M	
C	-x		n/a		+x		+x	
E	0.25 - x		n/a		x		x	

First, find the K_b from the K_a and K_w :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$$

Set up a K_b expression and solve for x.

$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]}$$
$$2.5 \times 10^{-11} = \frac{(x)(x)}{0.25 - x}$$
$$2.5 \times 10^{-11} \approx \frac{x^2}{0.25}$$
$$x = 2.5 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

Now find pOH and pH:

$$\text{pOH} = -\log(2.5 \times 10^{-6}) = 5.60_2$$
$$\text{pH} = 14 - 5.60_2 = 8.40$$

PRACTICE PROBLEM 5

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 1500. mL of 0.50 M NaOH are added.

— *answer* —

PRACTICE PROBLEM 5

You have a 1.0 L solution of 0.50 M HNO_2 ($K_a = 4.0 \times 10^{-4}$) being titrated with 0.50 M NaOH.

Calculate the pH of this solution after 1500. mL of 0.50 M NaOH are added.

— answer —

At this point, we have added a lot of NaOH, which is a strong base, so remember: $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

First, determine how much OH^- we have added:

$$n_{\text{HNO}_2} = 1.0 \text{ L} \times \frac{0.50 \text{ mol HNO}_2}{1 \text{ L}} = 0.50 \text{ mol HNO}_2 \quad n_{\text{OH}^-} = 1.500 \text{ L} \times \frac{0.50 \text{ mol OH}^-}{1 \text{ L}} = 0.75 \text{ mol OH}^-$$

We are past the equivalence point. Second, we need to consider the reaction between HNO_2 and OH^- using an ICF chart:

	HNO_2	+	OH^-	\rightarrow	NO_2^-	+	H_2O
I	0.50 mol		0.75 mol		0 mol		n/a
C	- 0.50		- 0.50		+ 0.50		n/a
F	0		0.25		0.50		n/a
	0 M		0.10 M		0.20 M		n/a

Convert to M
by dividing by
 $V_{\text{tot}} = 2.50 \text{ L}$

Because OH^- is a much stronger base than NO_2^- , we need only consider its effect on pH.

$$\text{pOH} = -\log(0.10) = 1.00$$

$$\text{pH} = 14 - 1.00 = 13.00$$