TITRATIONS

An Introduction

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It's your BIRTHDAY!

I'm going to make you birthday cupcakes. Every birthday cupcake has two candles in it, or:

1 cupcake + 2 candles → 1 birthday cupcake

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It's all about relationships…

I have 12 candles – how many cupcakes do I have?

NONE! Or 10… or 24… or 1000.
If there is no relationship between the candles and the cupcakes, there is no restriction on the amount of either one!
A "reaction" creates a relationship between different things. In the case of my "birthday cupcakes", there is now a relationship between cupcakes, candles, and birthday cupcakes – BUT ONLY IF I DO THE REACTION!

Suppose I have a drawer full of candles…

I'm too lazy to count the candles. I'm making birthday cupcakes anyway, so I just start baking cupcakes and keep baking them until I run out of candles. I baked 13 cupcakes, then I ran out of candles. How many candles did I have?

You probably arrived at 26 candles without even getting out your calculator. That is correct!

\[
\frac{2 \text{ candles}}{1 \text{ cupcake}} = 26 \text{ candles}
\]
1 cupcake + 2 candles \rightarrow 1 birthday cupcake

The reaction establishes a fixed relationship between the NUMBER of each thing in the reaction.

If I know one of the things in the reaction, I know them all.

I made 14 birthday cupcakes...well, I must have had 14 cupcakes and 28 candles:

\[
\begin{align*}
1 \text{ cupcake} & \quad \rightarrow \quad 14 \text{ birthday cupcakes} \\
2 \text{ candles} & \quad \rightarrow \quad 28 \text{ candles}
\end{align*}
\]

The REACTION connects everything.

I have to DO the reaction for the relationship to be fixed.

If I DO the reaction, however, and know how much of anything was used, I know how much of everything was used.

I used 50 candles...well, I must have had 25 cupcakes.

I made 100 cupcakes...well, I must have had 50 candles.

That is a titration!

Titrations are used to figure out how much of one compound you have by REACTING it with another compound.

The stoichiometry of the reaction creates a fixed ratio between the two reactants. So if I know how much of one of them there is, I know how much of BOTH of them there are!
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**Known vs. Unknown**

\[ A + 2B \rightarrow C \]

Well, if I add "B" to the sample, what will happen?

If I add 'B' to the sample, it should form "C" but only if...

...I have "A"

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So, I start with "5 As" in my beaker and then add B to it.

What happens?

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After I add 2 Bs, I get one C...
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After I add 4 Bs, I get two Cs...

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After I add 6 Bs, I get 3 Cs...

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After I add 8 Bs, I get 4 Cs...
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A + 2B → C

After I add 10 Bs, I get 5 Cs...

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A + 2B → C

After I add 1,000,000 Bs, I get 5 Cs.

As soon as I ran out of A, the amount of B becomes irrelevant! I can't make C without both A and B!

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Completion of the Reaction

A + 2B → C

So, if I think A is there, I can add known amounts of B. If I form C, then there was A there. If I gradually add more known amounts of B until I stop forming C, then I'll know how much A was originally there.

How much?
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**Equivalence Point**

A + 2 B → C

I stop making C when

Moles of B added = 2x moles of A original there!

This is called the equivalence point!

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**Titrations**

ALL titrations work the same way:

You have an unknown amount of one compound (call it A).

You have a known amount of a different compound (call it B).

You know a chemical reaction that occurs between A and B.

Add B until no more reaction occurs.

The amount of A is stoichiometrically equivalent to B!

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**The “tough part”:**

How do I know the reaction has stopped?

1. I get no new C.
2. I have no A left.
3. I have extra B left over.
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Watch A:

B
A

2 A

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Watch A:

B
A

1 A

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Watch A:

B
A

0 A! I'm DONE!
Or you could watch B

Watch B:

A

B

0 B

Watch B:

A

B

0 B
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Watch B:

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Watch B:

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Or you could watch C
Watch C:

Still 5 C! I'm DONE!

A and B are easier to watch…
...it's more obvious if there is none vs. some.
Acid/Base Titrations
How does this work for an acid/base titration?
What is the first thing we need to know?
EXACTLY! The Chemical Reaction

Acid-base Reaction
In an acid/base titration, the generic reaction is:

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \]
\[ \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2 \text{H}_2\text{O} \]

An acid is a proton donor (H⁺)
A base is a proton acceptor, is it always an OH⁻?
Does it matter?

As I make water, by adding OH⁻ to H⁺ (or H⁺ to OH⁻), the pH changes.

How do I know that I’m done adding…?

When I reach “equivalence” (I’m “done”), the pH should be…

7 (for strong acids/bases)
Indicators of the endpoint

- You can use a pH meter to monitor pH.
- You can use chemical indicators to monitor pH. Some dyes change color when the pH changes. If you add a little bit of one of these dyes that changes color around pH = 7, then it will change color when you reach equivalence.

Watch B:

pH is low

Watch B:

pH is getting higher
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Watch B:

B

A

pH is even higher

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Watch B:

B

A

pH is even higher

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Watch B:

B

A

pH is near 7
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Watch B:

B

A pH is 7

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Watch B:

B

A pH is over 7

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pH vs. mL Base added

pH

mL OH- added
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An example of titration.

I have a 25.00 mL sample of an acid of unknown concentration. After addition of 13.62 mL of a 0.096 M NaOH solution, equivalence was reached. What was the concentration of acid in the original wastewater sample?

Where do I start?

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Chemical Reaction:

H⁺ + OH⁻ → H₂O

At equivalence...?

Moles of H⁺ = Moles of OH⁻ added

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An example of titration.

I have a 25.00 mL sample of an acid of unknown concentration. After addition of 13.62 mL of a 0.096 M NaOH solution, equivalence was reached. What was the concentration of acid in the original wastewater sample?

What do I need to determine?

Moles of OH⁻ added!

How do I figure that out?

Molarity combined with volume!
The solution

13.62 mL NaOH = 0.01362 L NaOH added

1000 mL

0.096 M NaOH = 0.096 moles NaOH

1 L solution

0.096 moles NaOH × 0.01362 L = 1.308 × 10⁻³ moles NaOH

What does that number tell us?
How many moles of H⁺ were originally there!
1.308 × 10⁻³ moles NaOH added = 1.308 × 10⁻³ moles H⁺ in original sample

An example of titration.

I have a 25.00 mL sample of an acid of unknown concentration. After addition of 13.62 mL of a 0.096 M NaOH solution, equivalence was reached. What was the concentration of acid in the original wastewater sample?

1.308 × 10⁻³ moles H⁺ in original sample

Am I done?
Not quite. We need the concentration of acid:
How do I calculate that?
Molarity = moles/L

An example of titration.

I have a 25.00 mL sample of an acid of unknown concentration. After addition of 13.62 mL of a 0.096 M NaOH solution, equivalence was reached. What was the concentration of acid in the original wastewater sample?

1.308 × 10⁻³ moles H⁺ in original sample = 0.0523 M

0.02500 L original sample
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Basically the end…

You can actually summarize this in an algebraic relationship… but IGNORE ME NOW if you understand the way we just did it.

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Equivalence Point

If you have a reaction:

\[ i_A A + i_B B \rightarrow \text{products} \]

One way of stating the molar relationship in the titration is:

\[ i_B M_A V_A = i_A M_B V_B \]

\[ M_A V_A = \left(\frac{i_A}{i_B}\right) M_B V_B \]

Where \( M \) = molarity and \( V \) = volume and \( i = \) stoichiometric coefficient

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\[ i_B M_A V_A = i_A M_B V_B \]

This really just summarizes the calculation we did in multiply steps last time:

\[ M_A V_A = \text{moles A} \]

\[ \text{moles B} = \frac{M_B V_B}{M_A V_A} \]

\[ \text{moles B} = \frac{M_B V_B}{M_A V_A} \]

\[ \text{moles A} \]
A little example

A 10.00 mL sample of waste water is titrated to its phenolphthalein endpoint by addition of 36.32 mL of 0.0765 M NaOH. What is the pH of the original waste water sample?

NaOH + H+ = Na+ + OH-

[OH-] = [NaOH]

H+ + OH- = H2O

1*36.32 mL * 0.0756 M = 1*10.00 mL * X M

X = 0.2745 M

pH = - log [H+]

Does the [H+] = [acid]? What if it’s a polyprotic acid?

0.2745 M of what?

Of [H+] – we reacted the waste water with OH-, all we know is the equivalent amount of H+ – which is all we need to know to get the pH

We don’t actually know what the acid (or acid(s)) were or what their concentrations are, we just know the H+. But that’s OK, the H+ is the active part of the acid!

pH = - log (0.2745 M)

pH = 0.56
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**Another Little Problem**

Titration of 25.00 mL of a sulfuric acid solution of unknown concentration required 43.57 mL of 0.1956 M NaOH to reach equivalence. What is the concentration of the sulfuric acid?

What do you need to notice about this problem?
Sulfuric Acid (H$_2$SO$_4$) is a diprotic acid.

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**If it helps…**

…write the balanced equation (a chemist would).

H$_2$SO$_4$ (aq) + 2 NaOH (aq) → Na$_2$SO$_4$ (aq) + 2 H$_2$O (l)

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**Stoichiometry ALWAYS Matters**

1 * 43.57 mL * 0.1956 M = 2 * 25.00 mL * X M

X = 0.1704 M H$_2$SO$_4$

If you wanted to calculate the pH…?
You need to again consider stoichiometry: each H$_2$SO$_4$ gives 2 protons
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\[ 2\,[H_2SO_4] = [H^+] \]
\[ 2 \times 0.1704 \text{ M} = 0.3408 \text{ M H}^+ \]
\[ \text{pH} = -\log (0.3408) = 0.47 \]

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**Acid-base Reaction**

Acid + Base \( \rightarrow \) H\(_2\)O + salt

HA + MB \( \rightarrow \) H-B + MA

An acid is a proton donor (H\(^+\))

A base is any proton acceptor – where'd the OH\(^-\) come from?

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**Acid-base Reaction**

It could come from the base:

HCl + NaOH \( \rightarrow \) H\(_2\)O + NaCl

But, not all bases have an OH:

HCl + NH\(_3\) \( \rightarrow \)??

NH\(_4\) + H\(_2\)O \( \rightarrow \) NH\(_4\)OH

HCl + NH\(_4\)OH \( \rightarrow \) H\(_2\)O + NH\(_4\)Cl

You can always generate OH\(^-\) in water, because water can always act as an acid.
A little bitty problem...

A 10.00 mL sample of waste water is titrated to its phenolphthalein endpoint by addition of 36.32 mL of 0.0765 M NaOH. What is the pH of the original waste water sample?

(This is just another way to phrase the question.)

Solution

A 10.00 mL sample of waste water is titrated to its phenolphthalein endpoint by addition of 36.32 mL of 0.0765 M NaOH. What is the pH of the original waste water sample?

36.32 mL * 0.0756 M = 10.00 mL * X M

X = 0.2745 M

pH = -log [H⁺]

Does the [H⁺] = [acid]?

What if it’s a polyprotic acid?

0.2745 M of what?

Of [H⁺] – we reacted the waste water with OH⁻, all we know is the equivalent amount of H⁺ – which is all we need to know to get the pH
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\[ \text{pH} = - \log [H^+] \]
\[ \text{pH} = - \log (0.2745 \text{ M}) \]
\[ \text{pH} = 0.56 \]

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**Another Little Problem**

Titration of 25.00 mL of an unknown sulfuric acid solution required 43.57 mL of 0.1956 M NaOH to reach equivalence. What is the concentration of the sulfuric acid?

What do you need to notice about this problem?

Sulfuric Acid (H$_2$SO$_4$) is a diprotic acid.

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**If it helps...**

...write the balanced equation (a chemist would).

\[ \text{H}_2\text{SO}_4(\text{aq}) + 2 \text{NaOH(\text{aq})} \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2 \text{H}_2\text{O(\text{l})} \]

This is sometimes written as a “net ionic equation”:

\[ \text{H}^+(\text{aq}) + \text{OH}^-\text{(aq)} \rightarrow \text{H}_2\text{O(\text{l})} \]
Stoichiometry ALWAYS Matters

1 * 43.57 mL * 0.1956 M = 2 * 25.00 mL * X M

X = 0.1704 M H₂SO₄

If you wanted to calculate the pH…?

You need to again consider stoichiometry: each H₂SO₄ gives 2 protons.

2 [H₃SO₄] = [H⁺]

2 * 0.1704 M = 0.3408 M H⁺

pH = - log (0.3408) = 0.47

An example of titration.

I have a 25.00 mL sample of a wastewater. After addition of 13.62 mL of a 0.096 M NaOH solution, equivalence was reached. What was the concentration of acid in the original wastewater sample?
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The solution

(13.62 mL) (0.096 M) = (25.00 mL) (X M)

Is this correct?
Units! Units! Units!
M = moles/L
If I want moles, I need to have Volume in L.
But, since the only different is 10\(^{-3}\), if I have V=mL,
then I have mmoles (10\(^{-3}\) moles) on each side.

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The solution

(13.62 mL) (0.096 M) = (25.00 mL) (M\(_2\))

1.307 mmoles = 25.00 mL (M\(_2\))
M\(_2\) = 0.0523 M

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Titration problem

A 25.00 mL sample of wastewater of unknown pH is titrated
with a standardized 0.1011 M NaOH solution. It takes
16.92 mL of the NaOH to reach equivalence. What is the
pH of the original wastewater sample?
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\[ M_{\text{NaOH}}V_{\text{NaOH}} = M_{\text{H}_2\text{SO}_4}V_{\text{H}_2\text{SO}_4} \]
\[ (0.1011 \, \text{M})(16.92 \, \text{mL}) = M_{\text{H}_2\text{SO}_4}(25.00 \, \text{mL}) \]
\[ M_{\text{H}_2\text{SO}_4} = 0.06842 \, \text{M} \]
\[ \text{pH} = -\log [\text{H}^+] = -\log (0.06842) \]
\[ \text{pH} = 1.16 \]

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Another little problem

A 25.00 mL sample of wastewater of unknown pH is titrated with a standardized 0.1011 M H\(_2\)SO\(_4\) solution. It takes 16.92 mL of the sulfuric acid to reach equivalence. What is the pH of the original wastewater sample?

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\[ 2 \, \text{OH}^- + \text{H}_2\text{SO}_4 = 2 \, \text{H}_2\text{O} + \text{SO}_4^{2-} \]
\[ i_{\text{base}}M_{\text{OH}^-}V_{\text{OH}^-} = i_{\text{acid}}M_{\text{H}_2\text{SO}_4}V_{\text{H}_2\text{SO}_4} \]
\[ (2)(0.1011 \, \text{M})(16.92 \, \text{mL}) = (1) M_{\text{base}}(25.00 \, \text{mL}) \]
\[ M_{\text{base}} = 0.136 \, \text{M} \]
\[ \text{pOH} = -\log [0.136] = 0.86 \]
\[ \text{pH} = 14 - 0.86 = 13.14 \]
Weak acids

The pH of an acid/base titration at equivalence is not always 7. (I lied, I admit it!)

It's only 7 if it is a "strong acid" and a "strong base".

What does "strong" mean in this context?