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Chloride

What a difference a D makes!

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Chloride is not chlorine

Measuring chloride is acquiring information about a very different property of the water.

Chloride is about "salt content".

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Saltiness

The presence of chloride is not lethal to humans, but it is objectionable in water supplies.

Chloride is bad for plants if the concentration is too high... Why?

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Osmotic pressure

Does anyone know what osmotic pressure is?

Osmotic pressure is the pressure required to overcome the natural pressure exerted by a solution by virtue of having a concentration.

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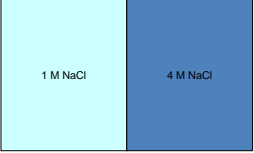
Why is it important?

Consider two solutions separated by a semi-permeable membrane (meaning water can pass through but nothing else) at room temperature (298 K).

On one side of the membrane is a 1 M NaCl solution. On the other side is a 4 M NaCl solution.

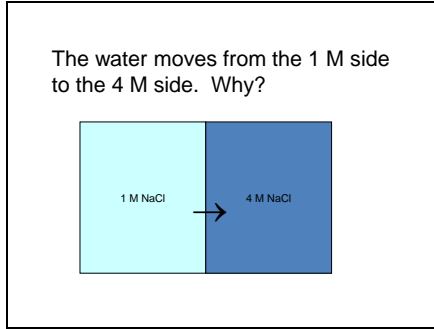
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What Happens?

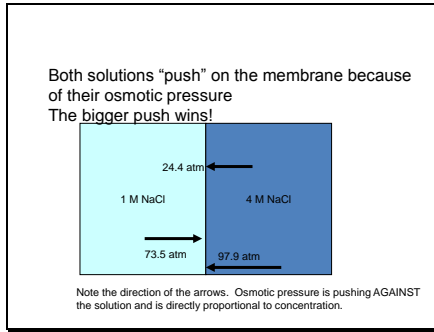


The diagram shows a rectangular container divided into two equal halves by a vertical line representing a semi-permeable membrane. The left half is filled with a light blue liquid and labeled "1 M NaCl". The right half is filled with a dark blue liquid and labeled "4 M NaCl".

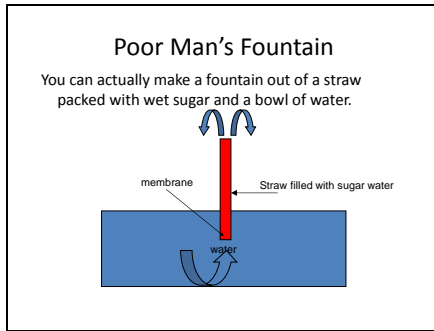
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Why is this bad for plants...?

Plants (and animals) are made up of little bags of aqueous solutions. Well, biologists call them "cells" but they really are just little membrane-bound aqueous solutions.

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Osmotic pressure

The water flows from the more dilute solution to the more concentrated solution.

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And if you're a plant...???

If the salt concentration in the soil (or water) is too high, water flows out of the plants not into them!!!!!!

Conquering armies used to "salt the fields". Add NaCl to the soil so that nothing would grow in it for years.

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Salt is bad, so...

We test for "saltiness" or chloride concentration.

Anybody want to guess how....???

Titration!

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Mohr Method – Titration with silver

All titrations require:

1. Reaction
2. Indicator

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Mohr Method – Titration with silver

$Ag^+_{(aq)} + Cl^-_{(aq)} \leftrightarrow AgCl_{(s)}$

$K_{sp} = 3 \times 10^{-10}$

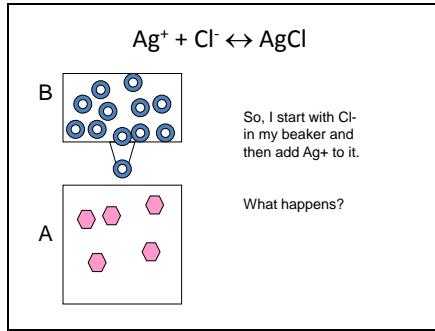
What would you see??

A white solid (AgCl) forms.

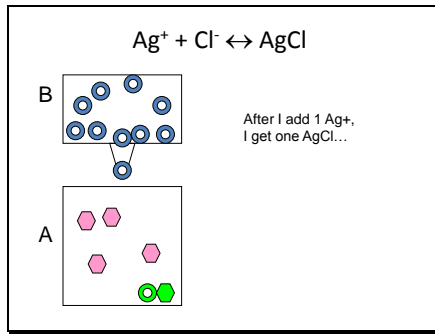
When is your titration done?

When the white solid stops forming.

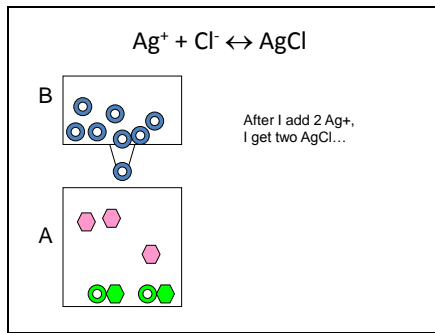
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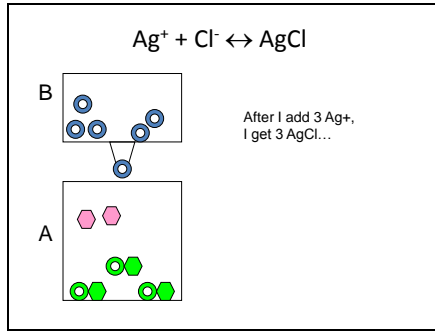
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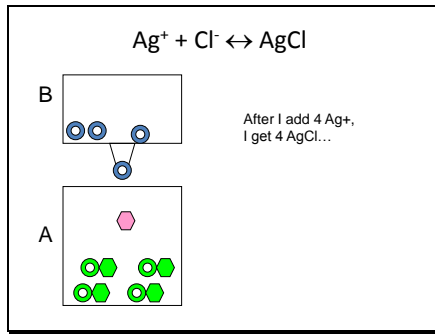
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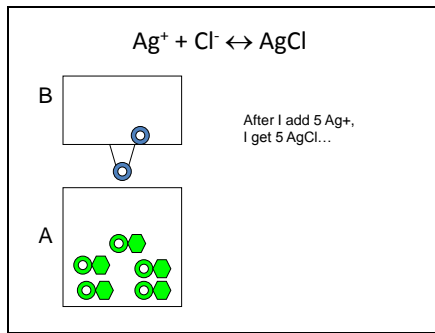
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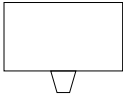
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$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl}$

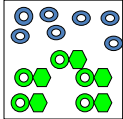
B



After I add 1,000,000 Ag^+ , I get 5 AgCl .

As soon as I made the 5 AgCl , I stopped making any new AgCl – that would be my endpoint!

A



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How would you know it's stopped?

Hard to tell. So we use a second reaction as an indicator. (Much like with the chlorine analysis.)

$$2 \text{Ag}^+_{(aq)} + \text{CrO}_4^{2-}_{(aq)} \leftrightarrow \text{Ag}_2\text{CrO}_4(s)$$

$K_{sp} = 5 \times 10^{-12}$

Silver chromate is a red-brown solid

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So you add a little chromate!

$$\text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \leftrightarrow \text{AgCl}(s)$$

$K_{sp} = 3 \times 10^{-10}$

$$2 \text{Ag}^+_{(aq)} + \text{CrO}_4^{2-}_{(aq)} \leftrightarrow \text{Ag}_2\text{CrO}_4(s)$$

$K_{sp} = 5 \times 10^{-12}$

Since the K is smaller and the $[\text{CrO}_4^{2-}]$ is small – the second reaction won't happen until the first one is done!

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$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl}$

B

A

So, I start with Cl^- in my beaker and my chromate indicator and then add Ag^+ to it.

What happens?

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$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl}$

B

A

After I add 1 Ag^+ , I get one AgCl ...

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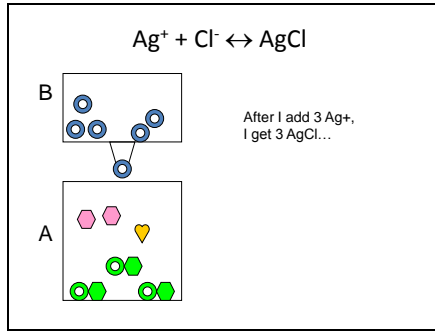
$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl}$

B

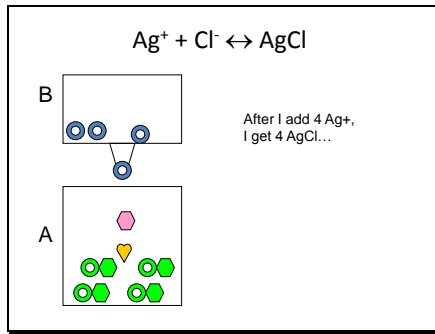
A

After I add 2 Ag^+ , I get two AgCl ...

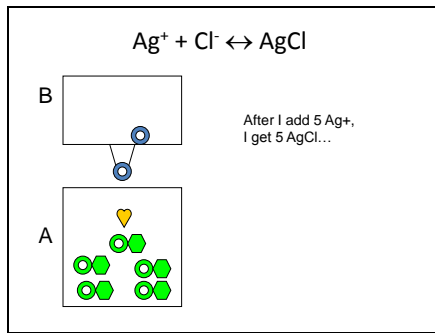
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$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl}$

After I add 6 Ag^+ ,
I get 5 AgCl and 1
 AgCrO_4 complex
which is red-
brown

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Mercuric Nitrate Method

It is also possible to react the chloride with mercury ($\text{pH} < 2.5$) - which is how you did the lab:

$$\text{Hg}^{2+}_{(\text{aq})} + 2 \text{Cl}^{-}_{(\text{aq})} \leftrightarrow \text{HgCl}_{2(\text{aq})}$$

Diphenylcarbazone will complex with Hg^{2+} to form a purple color.

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Sample problem

100.0 mL of waste water is titrated using the Mohr method. A chromate endpoint is reached after addition of 16.43 mL of 0.09762 M AgNO_3 . What is the chloride concentration in mg Cl/L?

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Solution

The Mohr titration has 1:1 stoichiometry

$$M_1V_1 = M_2V_2$$
$$M_1 (100.0 \text{ mL}) = (0.09762 \text{ M}) (16.43 \text{ mL})$$
$$M_1 = 0.01604 \text{ M Cl}^-$$

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Units! Units! Units!

mg/L is the more common unit for Cl^- concentration (as well as Cl_2 actually)

$$M_1 = 0.01604 \text{ M Cl}^-$$

How do I get the units right?

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Units! Units! Units!

$$M_1 = \frac{0.01604 \text{ moles Cl}^-}{1 \text{ L solution}}$$

We just need to convert moles to mg!

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Units! Units! Units!

$$\frac{0.01604 \text{ moles Cl}^-}{1 \text{ L solution}} * \frac{35.453 \text{ g Cl}^-}{\text{mole Cl}^-} * \frac{1000 \text{ mg}}{1 \text{ g}}$$

= 568.6 mg/L

(which is actually pretty high – anything above 250 mg/L will taste salty)

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Sample problem

100.0 mL of waste water is titrated using the Mercuric Nitrate method. A diphenylcarbazone endpoint is reached after addition of 16.43 mL of 0.09762 M $\text{Hg}(\text{NO}_3)_2$. What is the chloride concentration in mg/L?

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Solution

The Mercuric Nitrate titration has 2:1 stoichiometry

$$i_2 M_1 V_1 = i_1 M_2 V_2$$
$$1 M_1 (100.0 \text{ mL}) = 2 (0.09762 \text{ M}) (16.43 \text{ mL})$$
$$M_1 = 0.03208 \text{ M Cl}^-$$

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Units! Units! Units!

mg/L is the more common unit for Cl⁻ concentration (as well as Cl₂ actually)

M₁ = 0.03208 M Cl⁻

How do I get the units right?

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Units! Units! Units!

M₁ = 0.03208 moles Cl⁻
1 L solution

We just need to convert moles to mg!

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Units! Units! Units!

$$\frac{0.03208 \text{ moles Cl}^-}{1 \text{ L solution}} * \frac{35.453 \text{ g Cl}^-}{\text{mole Cl}^-} * \frac{1000 \text{ mg}}{1 \text{ g}}$$

= 1137.2 mg/L

(which is actually pretty high – anything above 250 mg/L will taste salty)
