HONORS CHEMISTRY LABORATORY

LABORATORY 4: TITRATION OF CHLORINE BLEACH

Household bleach contains an oxidizing agent known as sodium hypochlorite, NaOCl (an alternative formula is NaClO). NaOCl is prepared by bubbling chlorine gas into a sodium hydroxide solution. Part of the chlorine is oxidized to the hypochlorite ion, OCl^-, and some is reduced to the chloride ion, Cl^-. The excess hydroxide keeps the resulting solution strongly basic. An equation describing this process is:

$$Cl_2(g) + 2\ OH^- \rightleftharpoons ClO^- + Cl^- + H_2O$$

The ability of bleach to serve as an oxidizing agent is reported in terms of "available chlorine." Chemically, this is incorrect because the true oxidizing agent in chlorine bleach is the ClO^- anion, not $Cl_2(aq)$. Because both $Cl_2(aq)$ and ClO^- react with a similar stoichiometry, the term "available chlorine" allows the hypochlorite concentration to be calculated as if $Cl_2(aq)$ was actually present in the solution.

"Chlorine free" bleaches, typically marketed as safe for use with colors generally contain other oxidizing agents such as sodium perborate ($NaBO_3 \cdot 2\ H_2O$ or, alternatively, $NaBO_2 \cdot H_2O_2 \cdot H_2O$) which produce hydrogen peroxide, H_2O_2, when dissolved in water. These products are commonly referred to as oxygen bleaches. Clorox 2® is an example of an oxygen bleach. The mechanism of action of both chlorine and oxygen bleaches is a combination of chlorination and oxidation reactions. Since the active ingredients are oxidizing agents, they are reduced in the reactions which means they accept electrons from the compounds undergoing oxidation.

The chromophore or "color center" in most organic dyes or stains involves multiple bonds such as C=C or N=N groups. These dyes or stains absorb light in a visible region of the electromagnetic spectrum and reflect other visible colors. A blue dye absorbs red and therefore blue is reflected to our eyes. The purpose of using a bleach is to reduce these chromophores to single bonds through either oxidation or chlorination. If the stain or dye loses its ability to absorb a particular wavelength, then all wavelengths are reflected which gives rise to white as the observed color. When this occurs, light will be reflected by the material rather than absorbed and the material will seem to be both whiter and brighter.

One commonly used method for determining oxidizing agents in solution is termed an "iodometric titration". Iodide ion is a strong enough a reducing agent that many oxidizing agents can react completely with the iodide ion resulting in many useful iodometric processes. The usual procedure involves the addition of an excess of iodide ion to the oxidizing agent analyte which produces iodine, which can be titrated with standard sodium thiosulfate solution. The iodine-thiosulfate reaction is quite fast and the equilibrium is far to the product side.

In the hypochlorite titration, the following steps occur.

1. Iodide ion is added to an acidified hypochlorite ion solution which results in the iodide being oxidized to iodine.

$$ClO^- + 2\,I^- + 2\,H^+ \rightleftharpoons Cl^- + I_2 + H_2O$$

2. Iodine is slightly soluble in water (0.00134 mol/L at 25 ºC but is soluble in solutions containing iodide ion. Iodine forms the triiodide complex with iodide, $I_2 + I^- \rightleftharpoons I_3^-$, with an equilibrium constant greater than 500 at 25 ºC. Normally, excess potassium iodide is added to the reaction mixture to increase the solubility of iodine and to decrease its volatility. The triiodide ion is pale yellow in dilute solution, and red-brown color in more concentrated solutions.

3. The reaction of iodine with thiosulfate is fast and goes to completion. Iodine oxidizes thiosulfate to the tetrathionate ion:

$$I_2 + 2\,S_2O_3^{2-} \rightleftharpoons 2\,I^- + S_4O_6^{2-}$$

The red-brown color of the triiodide ion becomes pale yellow as the I_2 is reacted and eventually the solution will become colorless when all of the I_2 has reacted to form I^- ion. Since it is very difficult to see when the pale yellow color becomes colorless, a sharper end-point detection system is needed. Starch forms a dark bluish purple complex with the triiodide ion. Care must be taken to not add the starch until most of the I_2 has been reacted since at high concentrations, the starch may prevent the I_3^- from reacting. The starch indicator is added just before the end point of the titration when the solution still has a pale yellow color. The endpoint of the titration occurs when the bluish colored starch-I_3^- complex is destroyed and the solution becomes clear. If you are unsure of the color change, read your buret and add an additional drop of titrant. If there is no significant change in color, the end point had been reached at the previous reading.

Procedure

Record all data and observations directly in your notebook. You will be given an unknown bleach sample for your analysis. You are to report the weight percent (w/w) of the NaOCl in the sample. The unknown consists of an undiluted sample of commercial bleach. Be sure to handle the solution with care since it is strongly basic and reactive.

Pretreatment of the unknown bleach solution:

1. Tare a small plastic beaker on the analytical balance.
2. Take the beaker off the balance and add approximately 5 mL of bleach to the beaker. You will need approximately 4.00 grams of bleach solution. If you are not close to 4.0 grams, remove the beaker from the balance and add or remove a few drops until your mass of bleach is between 3.9 and 4.1 grams. Weigh the sample to the nearest ±0.0001g. Record the mass of your unknown bleach solution.
3. Carefully rinse the bleach solution into a 100-mL volumetric flask. If you lose any sample, you must start over. Try not to create excessive foam by letting the added water run down the side of the flask neck.

4. Rinse the beaker with several additional portions of distilled water and transfer the washings to the volumetric flask.
5. Fill the volumetric flask to the mark, stopper, and mix the contents well.

Titration of the unknown bleach sample:

1. Rinse the buret with a small portion of the standard thiosulfate solution and discard the solution. Fill the buret with the thiosulfate solution and record the initial volume.
2. Pipet 25.00 mL of the diluted unknown into a 125 mL Erlenmeyer flask. Add approximately 50 mL of distilled water, 2 g of solid KI and 10 mL of 0.5 M H_2SO_4 solution. A burgundy-yellow color indicates the presence of free iodine.
3. Add a stir bar to the flask and have the solution slowly mixing on a magnetic stirrer. Titrate with the standard thiosulfate solution until a pale yellow color is obtained, stop the titration and add 2 mL of 2% starch solution. Stir the solution well and you should observe a dark blue-black color. Continue the titration until one drop causes the dark color to disappear. The solution may or may not appear clear at this point. Record the final buret reading and calculate the total volume of titrant used.
4. Repeat the titration with another 25.00-mL sample of the diluted unknown.

Calculating the weight percent of sodium hypochlorite in your bleach solution:

The following is a sample calculation for determining the weight percent of sodium hypochlorite in your bleach sample. Make sure you correct your calculation back to the original amount of bleach.

Calculation of the Weight Percentage of Sodium Hypochlorite in an Unknown Bleach Sample by Titration with a Known Sodium Thiosulfate Concentration

define the weight of ~4.00 mL of the bleach solution	$mass_{bleach} := 4.1067 \cdot gm$
define the volume to which the bleach was diluted	$V_{dil} := 100 \cdot mL$
define the volume of the diluted sample taken for analysis	$V_{samp} := 25 \cdot mL$
define the concentration of the standardized thiosulfate solution	$C_{thio} := 0.0500 \cdot \frac{mole}{liter}$

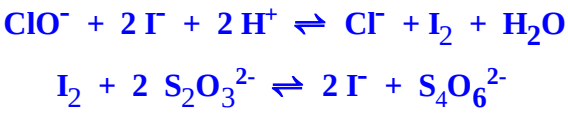
define the volume of thiosulfate solution that was used to titrate to the endpoint

$V_{thio} := 29.46 \cdot mL$

calculate the moles of thiosulfate used in the titration

$thio_{mol} := V_{thio} \cdot C_{thio}$

$thio_{mol} = 1.473 \times 10^{-3}\ mole$



$$ClO^- + 2\,I^- + 2\,H^+ \rightleftharpoons Cl^- + I_2 + H_2O$$

$$I_2 + 2\,S_2O_3^{2-} \rightleftharpoons 2\,I^- + S_4O_6^{2-}$$

since the stoichiometry of the reaction is 1:2, the moles of NaOCl = 2 × moles of $S_2O_3^{-3}$

calculate the moles of NaOCl titrated in the unknown sample

$NaOCl_{mol} := \frac{thio_{mol}}{2}$

define the molar mass of NaOCl

$MM_{NaOCl} := 74.442 \cdot \frac{gm}{mole}$

calculate the mass of NaOCl titrated

$mass_{NaOCl} := NaOCl_{mol} \cdot MM_{NaOCl}$

$mass_{NaOCl} = 0.0548\ gm$

calculate the total mass of NaOCl in the 5 mL of bleach taken for analysis

$mass_{unk} := mass_{NaOCl} \cdot \frac{V_{dil}}{V_{samp}}$

$mass_{unk} = 0.2193\ gm$

calculate the weight percentage of NaOCl in the 5 mL unknown bleach sample

$wtpct_{NaOCl} := \frac{mass_{unk}}{mass_{bleach}} \cdot 100$

$wtpct_{NaOCl} = 5.34$