Experiment 14A

FV 2/7/05

BOILER WATER CHEMICAL TESTS AND TREATMENTS

MATERIALS: Automatic zero burets, 100 and 10 mL graduated cylinders, 50-mL buret, 5-mL volumetric pipet, 10-mL graduated pipet, evaporating dish, 250 mL Erlenmeyer flasks, two 100-mL volumetric flasks, boiler water, 0.050 M HNO_3, 0.0050 M $Hg(NO_3)_2$, 0.0200 M $Na_2S_2O_3$, 2.0 M $MnSO_4$, 10.0 M KOH, 0.60 M KI, 0.060 M Na_2SO_3, 0.1 M $CoSO_4$, 18 M H_2SO_4, 2% starch solution, phenolphthalein, methyl purple, bromphenol blue, diphenylcarbazone (DPC), pH meter, thermometer, magnetic stirrer

PURPOSE: The purpose of this experiment is to demonstrate the chemical principles associated with some of the tests used for monitoring boiler water systems. These principles help guide the treatment of feed water for use in boiler water systems for minimizing scale formation and corrosion, e.g., using oxygen scavengers to remove dissolved oxygen.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Explain the process of an acid/base titration and the use of indicators.
2. Standardize and use a pH meter.
3. Explain the general purposes and chemical properties of indicators.
4. Convert concentration units of molarity to ppm (parts per million).
5. Predict the saturated concentration of dissolved oxygen in water using Henry's Law.
6. Describe a chemical treatment for removing dissolved oxygen from water.
7. Explain the process of a redox titration and the use of an indicator to determine the endpoint.

DISCUSSION:

Go to http://www.chemistry.usna.edu/manual/Ex14A_Boiler_Water_Background.pdf for background information on Navy Boiler water tests.

Indicators. There are two broad categories of indicators used in many chemical analyses: acid-base indicators and chemical indicators. Most indicators change color in response to changes in the titration solution. By selecting the appropriate indicator, one can have the indicator change color at a certain point in the titration (e.g., near the equivalence point in an acid/base titration). Obviously, indicators must be molecules which absorb different wavelengths of light depending on the chemical state of the indicator.

Acid-Base Indicators. Acid-base indicators are generally organic weak acids where the neutral acid form absorbs one set of wavelengths (hence, makes solutions appear a certain color), and the conjugate base form absorbs a different set of wavelengths (hence, makes solutions appear a different color). As with the all weak acids, there is an associated acid dissociation constant, K_a^{In}, associated with the equilibrium:

$$HInd_{color1} + H_2O(l) \leftrightarrow Ind^-_{color2} + H_3O^+ \qquad (1)$$

The equilibrium constant expression, including reference to the colors of the acid and conjugate base forms, is

$$K_a^{In} = [H_3O^+]\frac{[Ind^-_{color2}]}{[HInd_{color1}]} \tag{2}$$

Normally, indicators are added to a solution in such small quantities that the impact on the acidity of the solution is negligible. However, the pH of the solution to which the indicator has been added has a significant impact on the predominant form of the indicator, and hence on the color of the solution. This is best illustrated by transforming Equation 2 to the following form:

$$pH = pK_a^{In} + \log\left(\frac{[Ind^-_{color2}]}{[HInd_{color1}]}\right) \tag{3}$$

From this equation, we see that if the pH of the solution is, for example, 1 unit higher than the pK_a^{In}, the concentration of the conjugate base form of the indicator, In^-, will be ten times larger than that of the acid form, HIn. For this case, the solution will appear to be color 2. Similarly, if the pH of the solution is 1 unit lower than the pK_a^{In}, the acid form will be ten times more concentrated than the base form, with the solution appearing to be color 1. If the pH of the solution were ~ pK_a^{In}, the solution would be a mixture of color 1 and color 2. During the course of a titration, if the pH of the solution were to change from one unit below the pK_a^{In} to one unit above, the solution's color would change from color 1 to color 2. From this, we see that a given acid-base indicator "indicates" when the pH of a solution changes from pH values just below its particular pK_a^{In} to those just above it.

There are hundreds of different indicators, each with a unique value of K_a^{In}. The selection of an indicator for use in a particular titration depends on the value of pH at which the color change is needed. For example, if the indicator were intended to "indicate" the equivalence point of a titration, an indicator whose pK_a^{In} value was close to the pH of the equivalence point would be selected, as illustrated in Figure 1.

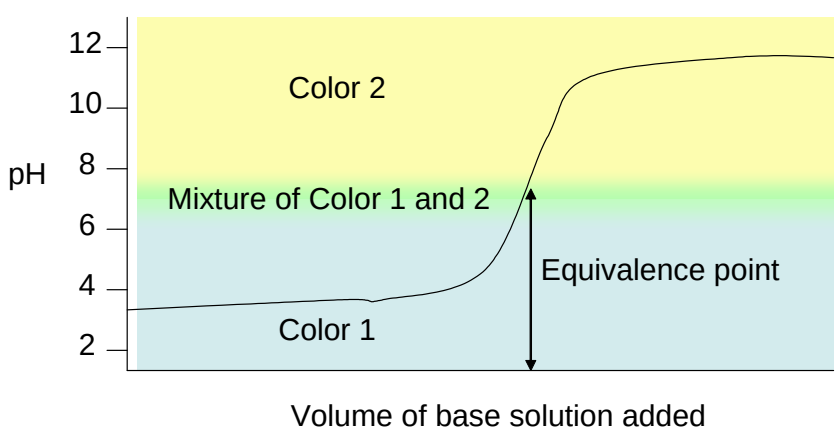
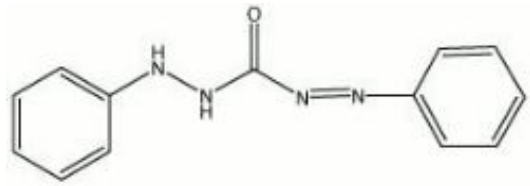


Figure 1. The equivalence point for this acid/base titration occurs at pH ~ 7. The indicator shown changes color between pH ~ 6 (it is blue below pH ~ 6) and pH ~ 8 (it is yellow above pH ~ 8). The pK_a^{In} of this indicator is about 7, and is therefore ideal for signaling this particular equivalence point. When the pH is between 6 and 8, the two colors are mixed together, yielding green.

Other chemical indicators. The same principle of color changes applies to other indicators as well. For example, consider the following indicator molecule, diphenylcarbazone (DPC):



which is used in titrations for determining the amount of Cl^- ion present in a sample. This molecule, when dissolved in water, is colorless. However, when Hg^{2+} ions are present, a complex ion ($Hg(DPC)^{2+}$) forms, which gives the solution an intense purple color. Since Hg^{2+} ions also react with Cl^-, the DPC indicator is a good candidate for use in a titration of Cl^- with Hg^{2+}. If Hg^{2+} ions are added to a solution containing both Cl^- ions and a small amount of DPC, the following reaction occurs:

$$Hg^{2+} + 2\ Cl^- \rightarrow HgCl_2(aq) \qquad (4)$$

Because Hg^{2+} binds more readily to Cl^- (if Cl^- is available), the DPC is in the uncomplexed state and colorless. However, upon complete reaction of the Cl^- ions, the next drop of Hg^{2+} solution will cause the following reaction to occur:

$$Hg^{2+} + DPC \rightarrow Hg(DPC)^{2+} \qquad (5)$$

The appearance of the purple color associated with the complex species $Hg(DPC)^{2+}$ is sudden and indicates that the Cl^- ions have completely reacted. Of course, in order for this to work, the Hg^{2+} ions must preferentially react with Cl^- over the DPC molecules, since both species must be present.

This DPC indicator, as a side note, only displays this color change if the overall solution environment containing the Cl^- is acidic, at a pH value of about 3 or below. Bromphenol Blue is an acid-base indicator which is yellow at pH values below 3 and blue at pH values above 4. In practice, a sample containing Cl^- is acidified first. The Bromphenol Blue plays the role of simply assuring that the pH for the entire Cl^- test system is 3 or below. Once this is satisfied, the yellow color of the Bromphenol Blue is constant. It is the intensity of the $Hg(DPC)^{2+}$ complex ion which overwhelms this relatively weak yellow color, causing the solution to appear purple, as indicated above.

Removing Oxygen from Water. One of the key steps in minimizing corrosion in a boiler is the removal of dissolved oxygen from the feedwater. This can be accomplished through both physical and chemical means.

Deaeration: Henry's Law and Temperature Effects on Gas Solubility. All dissolved gases obey Henry's Law, which for the case of oxygen, is:

$$[O_2] = K_H P_{O_2} \qquad (6)$$

where P_{O_2} is the partial pressure of oxygen gas above the solution and K_H is the Henry's Law constant for oxygen in an aqueous solution. In addition, all dissolved gases become less soluble in water at higher temperatures. A water sample can be physically deaerated (i.e., have its dissolved oxygen removed) by first heating the water, and then reducing the pressure of gas above the water, as with a vacuum system.

Fortunately, a sample of water which has been deaerated will, if reexposed to the normal atmosphere, take several hours to become saturated with dissolved oxygen again.

A nomogram is a simple chart which enables the user to determine the percent saturation of dissolved oxygen in water for any temperature. It cleverly combines the pressure and temperature dependence of the solubility of oxygen into one chart. A simple, automated nomogram for dissolved oxygen can be found within the document at the following website:

http://www.gvsu.edu/wri/education/manual/oxygen.htm

Oxygen Scavengers. Physical deaeration is effective at removing the majority of dissolved oxygen in a water sample. However, chemical means are required to remove the remainder of the dissolved oxygen. There are many types of oxygen scavengers which are used in actual boiler water treatment schemes. This experiment focuses on the use of the sulfite ion, which is known to react with dissolved oxygen according to:

$$2\ SO_3^{2-}(aq) + O_2(aq) \rightarrow 2\ SO_4^{2-}(aq) \qquad (7)$$

In principle, addition of some Na_2SO_3 solution to a water sample should result in oxygen removal. However, the rate of this reaction is extremely slow. For practical purposes, therefore, a catalyst is required in order to effectively use sulfite ion as an oxygen scavenger. The Co^{2+} ion acts as a catalyst for this reaction, based on the following two-step process:

$$O_2 + 4\ Co^{2+} + 2\ H_2O \rightarrow 4\ Co^{3+} + 4\ OH^- \qquad (8)$$

$$2\ Co^{3+} + 2\ OH^- + SO_3^{2-} \rightarrow SO_4^{2-} + 2\ Co^{2+} + H_2O \qquad (9)$$

The net result of the two-step process is the same as Equation 7 above, but the rate at which it occurs is much faster.

Since the sulfite ion, SO_3^{2-}, is a medium-strength conjugate base of a weak acid, whereas the sulfate ion, SO_4^{2-}, is an extremely weak base, the progress of the oxygen scavenging can be detected through the use of a pH meter. As the sulfite ion is consumed in Equation 7, the pH of the water sample will steadily fall.

PROCEDURE:

1. Your instructor will demonstrate the use of the following laboratory equipment: (a) a pH meter, including standardizing the meter and taking measurements of pH; (b) an automatic zero buret. Make any notes for future reference.

Phosphate Acid-Base Titration

2. To a 100 mL sample of boiler water in an evaporating dish, add two drops of phenolphthalein indicator, and titrate with 0.050 M HNO_3 from an automatic-zero buret. Immediately after the color change, add two drops of methyl purple and continue on with the titration until the next color change. Record all relevant data.
3. Identify the major chemical species present in the evaporating dish at the following points of the titration: (a) before the titration begins, (b) at the point of the first color change, and (c) at the point of the second color change. Write the chemical reactions which correspond to the two stages of the titration.
4. Using available pipets and flasks, prepare 25.0 mL of HNO_3 solution which is 1/5 as concentrated as the 0.050 M HNO_3 in the automatic zero buret. Place this solution in a buret.

5. Repeat step 1 above, with the following modifications: (a) place the 100-mL sample of boiler water in a 400-mL beaker instead of an evaporating dish, (b) use the diluted HNO_3 solution from the buret, and (3) place the pH meter probe in the boiler water sample throughout the titration. Also, use the magnetic stirrer to assure thorough mixing throughout the titration. Take pH readings and note the color at approximately 0.5 mL intervals during the titration. Use the same indicators as before, adding them at the same points of the titration.
6. Determine the molarity and the ppm of (a) phosphate ions and (b) hydrogen phosphate ions in the original boiler water sample. Use Excel to produce a clearly labeled titration curve.

Chloride Ion Test

7. Add about 1 mL of 0.050 M HNO_3 to about 25 mL of boiler water in a clean beaker. Using small amounts of acidified boiler water, the $Hg(NO_3)_2$ solution, and the diphenylcarbazone (DPC) solution, prove that the Hg^{2+} ions preferentially react with the Cl^- rather than the DPC. Deposit all solutions containing Hg^{2+} ions in a waste bottle in the instructor's hood.
8. To a 25.0 mL sample of boiler water in an evaporating dish, add 5 drops each of bromphenol blue and diphenylcarbazone (DPC). Add drops of 0.050 M HNO_3 until the solution turns pale yellow. Then add 1 additional mL of HNO_3 solution. Re-zero and titrate this acidified boiler water with 0.0050 M $Hg(NO_3)_2$ solution until the color change. Deposit all solutions containing Hg^{2+} in a waste bottle in the instructor's hood.
9. Determine the molarity and the ppm of Cl^- in the original boiler water sample.

Dissolved Oxygen Test and Treatment

10. Fill a 100-mL volumetric flask to the mark with distilled tap water (NOT boiler water). Measure and record the temperature of the water. Add 10 drops each of 10 M KOH and 2 M $MnSO_4$ solutions. Stopper the flask, shake gently, and set aside for at least 5 minutes. Now add 10 drops of 0.60 M KI and 20 drops of 18 M H_2SO_4 solutions. Stopper again and swirl until all of the solid material disappears. Pour the solution into a 250-mL Erlenmeyer flask, including any rinsings to assure complete transfer. Titrate with the 0.020 M $Na_2S_2O_3$ solution until a pale yellow color remains. Add a few drops of starch solution, and continue titrating until the blue color permanently disappears.
11. Determine the molarity and ppm of dissolved oxygen in the distilled tap water sample.
12. Place 100 mL of distilled tap water in a 400 mL beaker. Based on the results from Step 11, determine how many mL's of 0.060 M Na_2SO_3 would be required to completely scavenge the dissolved oxygen. Add about ½ of this amount to the water (assume that there are 20 drops of aqueous solutions per mL). Place the probe of the pH meter in the treated water sample and measure its pH over a period of one or two minutes. Add 1 drop of 0.1 M $CoSO_4$ solution, swirl gently, and continue monitoring the pH of the mixture. How do your observations prove that dissolved oxygen is reacting with the sulfite ion, thereby resulting in a lowering of the dissolved oxygen concentration in the water? What was the effect of adding the Co^{2+} catalyst?
13. Repeat Step 10 above, with the following modifications:
    a. Prior to adding the KOH and $MnSO_4$ solutions, add about ½ of the amount of SO_3^{2-} ions that would be required to completely scavenge the dissolved oxygen (as in Step 12), along with 1 drop of the Co^{2+} catalyst. After waiting a minute, repeat the remainder of Step 10.
14. Determine the molarity and ppm of dissolved oxygen after the oxygen scavenger treatment. Are these results consistent with your expectations, based on how much scavenger reactant you added to the water sample?

QUESTIONS FOR CONSIDERATION:

1. Explain why the unit "ppm" is essentially the same as the unit "mg/L" for aqueous solutions.

2. Explain why the phenolphthalein indicator does not interfere with the methyl purple indicator in the second stage of the phosphate titration.

3. The K_a s for phenolphthalein and methyl purple are 5.5×10^{-10} and 7.9×10^{-6}, respectively. Show why these indicators are good choices for detecting the equivalence points of this titration.

4. Based on your data, determine the ratio of the concentrations of the phosphate ion and the hydrogen phosphate ion in the original boiler water sample. What would the Henderson-Hasselbalch equation yield for the pH of this boiler water sample, based on this ratio? How does this compare to the measured pH of the boiler water sample? [Note: the Henderson-Hasselbalch equation is not valid in this case due to the fact that the phosphate ion is a very *strong* "weak" base.]

5. Explain why it isn't *necessary* to add the bromphenol blue indicator in order to determine the amount of chloride ion using DPC as an indicator.

6. Using the nomogram for dissolved oxygen in water referred to in the Discussion section, determine the percent saturation of the water sample tested.

7. Based on tabulated values of K_a and/or K_b, predict the pH of a water sample immediately after adding the Na_2SO_3 solution, as in step 12. How does this compare to the measured pH?

8. Identify the catalyst and any intermediates associated with the two-step mechanism in Equations 8 and 9 in the Discussion section.

9. The rate for redissolving oxygen gas in water is very slow. Why is this fact helpful when doing experiments which measure the amount of dissolved oxygen in water?

10. Discuss the negative consequences if Cl^- levels or dissolved O_2 levels are not kept to a minimum in a boiler water system.

11. Discuss two positive effects that the phosphate/hydrogen phosphate ions have on a boiler water system.