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## II. Redox Chemistry

### II.1- Tollen's Test for Aldehydes and Ketones (a.k.a. The Silver Mirror)

#### Background

Silver (I) is reduced to silver metal by aldehydes, but not by ketones. Dextrose (D-glucose, a monosaccharide) is a polyhydroxyaldehyde which reduces silver.

In solution, either  $\alpha$ - or  $\beta$ -D-glucose (see figure II.2.1 below), undergoes a slow equilibrium with the open-chain form and with the other anomer. This equilibrium is called *mutarotation*.

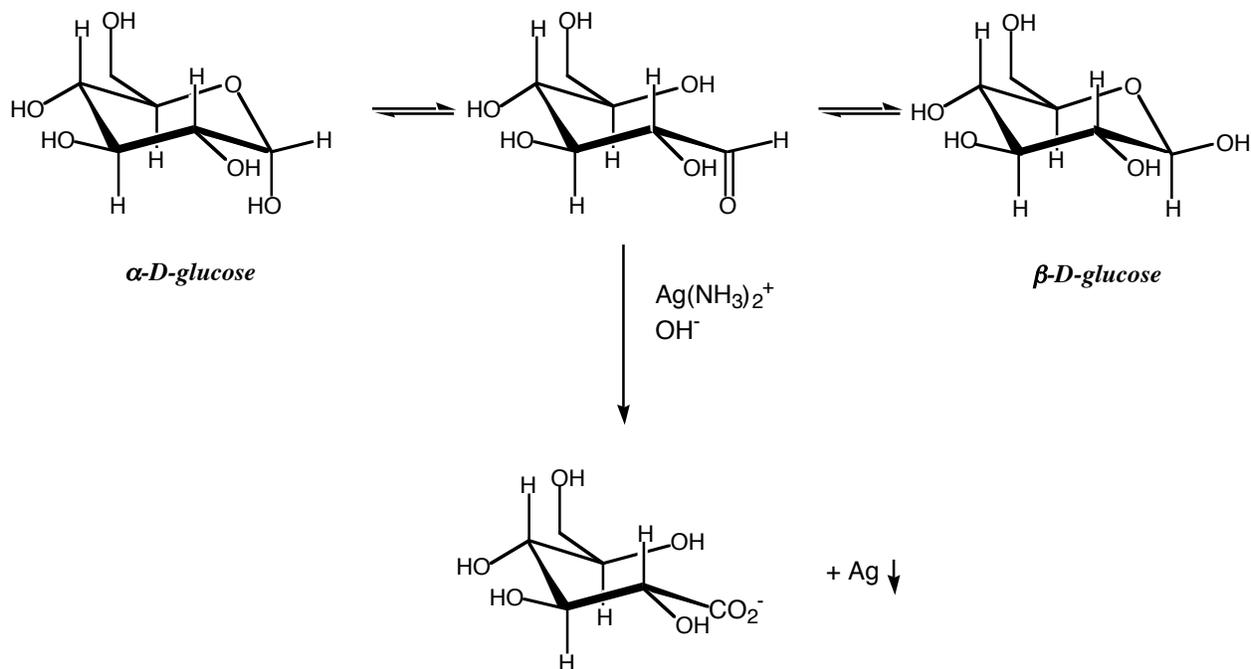
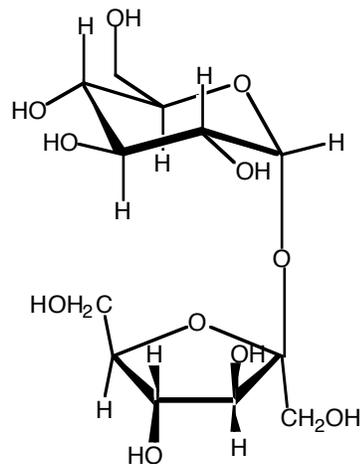


Figure II.2.1

Sucrose on the other hand, is a disaccharide, a combination of glucose and fructose (figure II.2.2) in which both anomeric carbon atoms are used in the glycoside link. Therefore, sucrose in water is not in equilibrium with an aldehyde or keto form, and does not exhibit mutarotation and thus is not a reducing sugar. Sucrose however breaks down in the basic Tollen's Reagent and the resulting glucose will reduce the silver.



*sucrose*

*β-D-fructofuranosyl α-D-glucopyranoside*

**Figure II.2.2**

**Materials:**

- Two 15mL test tubes.
- Nitric Acid (HNO<sub>3</sub>)
- Distilled water
- 0.1 M Silver Nitrate (AgNO<sub>3</sub>)
- Concentrated Ammonia (NH<sub>3</sub>)
- 0.80 M Potassium Hydroxide (KOH)
- 0.25 M Glucose
- 0.25 M Sucrose

**Safety:** Concentrated nitric acid and concentrated ammonium hydroxide are highly corrosive and will cause severe burns. Vapors are harmful. Nitric acid is also a powerful oxidizing agent that may ignite or react explosively with many inorganic and organic substances. Potassium hydroxide solutions are irritating and may cause burns depending upon the concentration and length of exposure. Acetone is volatile and highly flammable. Do not use near a heat source. Silver nitrate solutions are irritating and oxidizing. Carry out the experiment in a well-ventilated hood.

**Procedure:**

- Rinse the test tubes with distilled water, nitric acid, water, acetone, and water in that order.
- Add 5 mL of 0.1 M silver nitrate to each test tube.
- Pour small amounts of ammonia to the silver nitrate solution and swirl until the solution is a brown color (muddy).
- Keep adding ammonia to this muddy mixture until it becomes colorless and clear again.

- Add about 2.5 mL of Potassium Hydroxide. If the solution becomes muddy (and remains after mixing), add more ammonia until the solution becomes colorless and clear again.
- To one test tube add 5 mL of glucose. To the other add 5 mL of sucrose. (Label test tubes first)
- At the same time, place the test tubes in a **hot** water bath.
- Swirl the tubes lightly and record your observations.

**Clean-Up:** The chemical waste should be disposed in the designated containers.

**Discussion:** Write the balanced chemical equations for all processes, including for the addition of ammonia and potassium hydroxide.

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## II.2- The Copper Mirror

### Background

Copper is widely distributed in Nature as metal, in sulfides, arsenides, chlorides, carbonates, etc. Copper is also the third most abundant metallic element in the human body, following iron and zinc, and it is important in all other life forms. Copper-containing biomolecules like *azurin* and *plastocyanin* found in algae and green leaves, participate in electron transfer reactions. *Hemocyanin*, found in molluscs, functions as an oxygen carrier. *Cytochrome c oxidase*, found in mitochondria, participates in the interconversion between water and oxygen. The biochemistry of copper relies primarily in its oxidation-reduction chemistry.  $\text{Cu}^{2+}$  in solution can be reduced to metallic copper by the addition of a strong reducing agent, such as hydrazine ( $\text{N}_2\text{H}_4$ ). The oxidation products of hydrazine are strongly dependent on the pH of the solution, the temperature, the oxidizing agent used and the catalytic impurities present:

### Materials:

- One large test tube
- 5 mL of 1M copper sulfate ( $\text{CuSO}_4$ ) solution
- 1 mL of 85% hydrazine hydrate solution

**Safety:** Hydrazine hydrate solutions are toxic, a suspected carcinogen, highly reactive and highly flammable. Symptoms of exposure include burning sensation, coughing, shortness of breath, headache, nausea. Carry out the experiment in a well-ventilated hood.

### Procedure:

- Rinse the test tube with distilled water, nitric acid, distilled water, acetone, and distilled water in that order.
- Add 5 mL of copper solution to the test tube, followed by 1 mL of hydrazine hydrate solution. Swirl once. The blue solution will immediately turn to a brownish-green.
- Immediately place the test tube in a hot water bath.
- Swirl the tube lightly and record your observations.
  
- To remove copper from the test tube walls use 1 mL (20 drops) concentrated nitric acid. Record your observations. Add 3 mL of water. Record your observations.

**Clean-Up:** The chemical waste should be disposed in the designated containers.

**Discussion:** Write the balanced chemical equations for all processes.

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## II.3- Oxidation States of Vanadium: Reduction of V<sup>5+</sup> to V<sup>2+</sup>

### Background

It is known that vanadium in extremely small amounts is a nutritional requirement for many types of organism, possibly including higher animals. The longest known example of vanadium in biochemistry is the accumulation of vanadium by certain lower marine organisms called tunicates. They concentrate vanadium by a factor of  $\sim 10^6$  over its level in the surrounding marine environment.

Vanadium exhibits an extended redox chemistry and can exist in several different oxidation states, each with a characteristic color.

### Materials:

- Mercury zinc amalgam
- Ammonium metavanadate solution

**Safety:** Mercury zinc amalgam is toxic, keep under aqueous solution.

### Procedure:

- Place 5 grams of zinc amalgam in a 125mL Erlenmeyer flask.
- Add 20 mL of vanadium solution. The solution should be yellow. Pour a small amount in a small testtube as a reference.
- Stopper the flask and gently swirl the solution. Record any color changes. Pour a small amount in a small testtube as a reference. (Hint: yellow + blue = green)
- Swirl the flask again and record any color changes. Save a small amount in a small testtube as a reference.
- Swirl the flask vigorously until another color change is observed.
- Compare all the colored solutions. Have the instructor or TA check the final color.
- Optional: Collect UV-VIS spectra on the colored solutions.

**Clean-up:** The chemical waste should be disposed in the designated containers.

### Discussion:

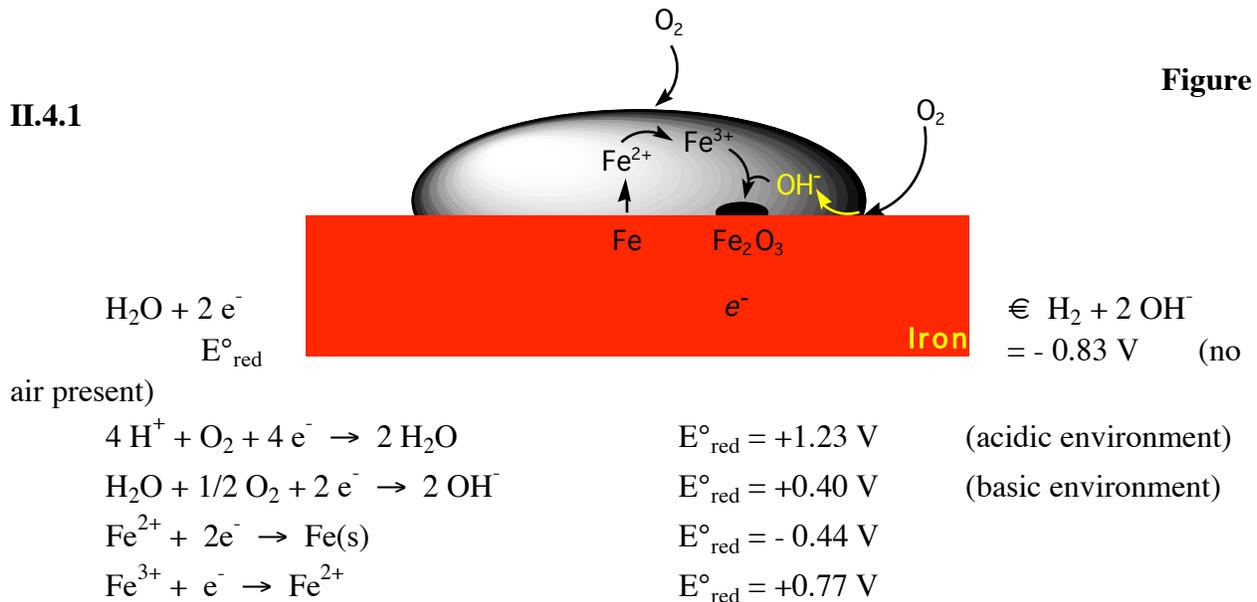
- Write the balanced chemical equations for each reduction step. Identify the colored species.
- Provide the oxidation state and the d electron count for each vanadium species.
- Arrange the vanadium species in order of increasing crystal field splitting.
- Can V<sup>5+</sup> and V<sup>4+</sup> exist free in aqueous solution? Why?

## II.4- Corrosion

### Background

Corrosion reactions are redox reactions in which a metal is attacked by some substance in its environment and converted to an unwanted compound. Corrosion cuts short the lifetimes of steel products such as bridges and automobiles, and replacing corroded metal parts cost billions of dollars a year: about 20 percent of the iron produced annually in this country is used to replace iron objects that have been discarded because of rust damage. Rusting of iron is known to require oxygen and water. The rusting process is summarized in the following figure (figure II.4.1):

II.4.1



**Materials:**

Solution A: contains  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $\text{NaCl}$ , and phenolphthalein.

Iron metal plate

scotch brite pad to clean metals

**Procedure:**

- Clean one of the surfaces of the iron plate with scotch brite.
- Place a drop of Solution A.
- Set aside and record your observations.

**Clean-up:** Rinse the iron plate under running water.

**Discussion:**

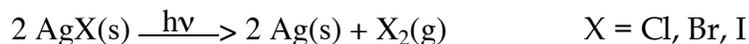
- Draw a scheme showing your observations.
- Write the balanced chemical equations for all processes. Identify the colored species.
- What are the oxidized and reduced species? Identify the anode and the cathode reactions.
- What's the function of the hexacyanoferrate(III),  $\text{NaCl}$ , and phenolphthalein?
- How can corrosion be avoided?

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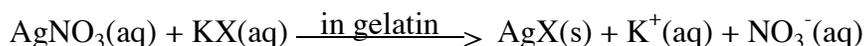
## II.5- Photography - Cyanotypes<sup>1</sup>

### Background-Black and White Photography

The earliest photographic (1830's) processes relied on printed out silver which requires long exposure times:



In the 1840's the "latent" image was discovered. AgI was used as the silver halide and the "invisible" latent image was chemically developed. This greatly shortened exposure times and became the basis for modern black and white photography:



This reaction produces a colloidal suspension of AgX in a gelatin solution.

It is ripened (heated) to increase particle size of silver halide.

A hardener is added to stiffen the gelatin.

The gelatin is then coated onto a support such as:

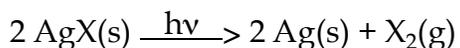
glass plate (1800's).

cellulose nitrate (fire hazard!!!) or acetate (safety film) for negatives.

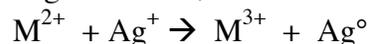
paper coated with baryta ( $\text{BaSO}_4$ ) for prints.

The gelatin is allowed to harden.

NOTE: the crystal structure and size of the silver halide crystals greatly affects light sensitivity of the film, and the sharpness of the image



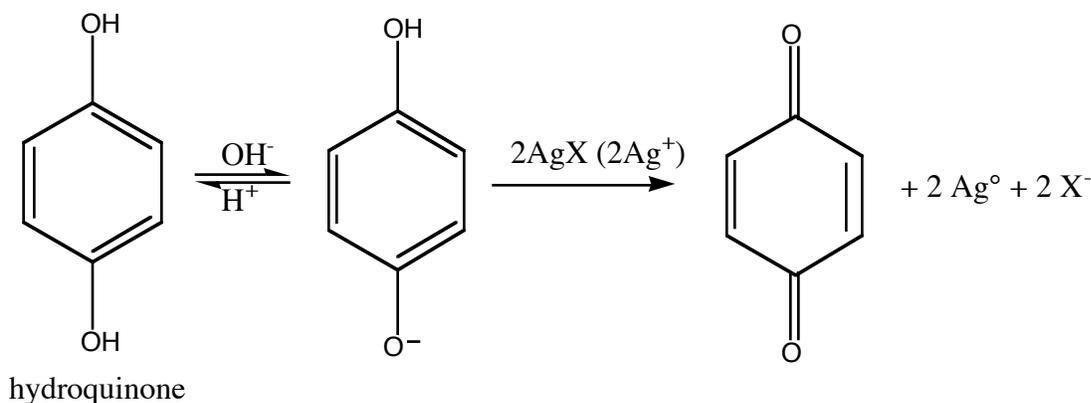
To make the latent image viewable, use a metal reducing agent such as  $\text{V}^{2+}$  or  $\text{Fe}^{2+}$ .



Or, more typically, use an organic reducing agent such as hydroquinone.

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<sup>1</sup> This experiment is adapted from an experiment developed by Prof. Pradip Malde The University of the South as part of National Science Foundation ILI grant DUE-9153695.



Note: the reaction requires base to proceed.

To stop the reaction, take advantage of the acid-base equilibrium by adding "stop bath" (acetic acid) to shift to the acid form of hydroquinone which is not readily oxidized.

The print or negative is "fixed" as discussed in solubility equilibria by using "hypo"  $\text{Na}_2\text{S}_2\text{O}_3$  to remove unreacted  $\text{AgX}$ .

### Background - Cyanotypes

In 1842, after the discovery of the photosensitivity of ferric ( $\text{Fe}^{3+}$ ) salts, Sir John Herschel invented the cyanotype process. This process involves coating a sheet of paper with a yellow light sensitive solution of ferric ammonium citrate and potassium ferricyanide. Exposure to UV light reduces ferric ( $\text{Fe}^{3+}$ ) salt to the ferrous ( $\text{Fe}^{2+}$ ) state and ferricyanide (the  $\text{Fe}^{3+}$  in  $[\text{Fe}(\text{CN})_6]^{3-}$ ) to ferrocyanide ( $\text{Fe}^{2+}$  in  $[\text{Fe}(\text{CN})_6]^{4-}$ ). The result is formation of a yellow blue image consisting of ferrous ferrocyanide. Washing removes the yellow soluble, unreduced (unexposed) salts, leaving behind an insoluble blue and white image. The image intensifies with time as ferrous ferrocyanide is oxidized to the deep blue color of ferric ferrocyanide, also known as the artist's pigment Prussian blue. The rate of oxidation can be increased by treating the image with an oxidizing solution.

### Procedure

**I. Stock solutions:** Prepare solutions at least 24 hours before coating paper and store in air tight brown bottles.

- Solution A:** 50 mL distilled water at  $\sim 21^\circ\text{C}$   
 10.0 g Ferric ammonium citrate (green is preferable to brown)
- Solution B:** 50 mL distilled water at  $\sim 21^\circ\text{C}$   
 4.0 g Potassium ferricyanide

## II. Sensitize the paper:

**A. Choice of paper:** To get good image resolution choose a paper that has

- 1) A smooth 'hot pressed' (HP) surface.
- 2) A high cotton or alpha-cellulose content.
- 3) An internal sizing agent, ideally with a pH of 7-7.5.
- 4) No alkaline buffering agents. Paper pH < 7.
- 5) Good wet strength (i.e. heavier weights of paper i.e., 160-200 g/m<sup>2</sup>).
- 6) No other additives such as fillers, brighteners, retention aids, dyes, bleaches, wet-strengthening agents...

Note: All papers have a 'felt' or 'blanket' side and a 'wire side'. The felt side generally has a more random texture and a less intrusive texture. Paper is a chemical entity in its own right and each type of paper (and sometimes each batch of a paper) will behave in its own way with the chemicals.

**B. Choice of room light conditions:** Work with the solutions and sensitized paper under tungsten light. Daylight and fluorescent light will expose/fog the paper.

### C. Paper preparation:

1. Cut the paper to leave a margin of at least an inch around the area to be coated to permit handling.
2. Lightly pencil guide marks to indicate the area to be coated on the sheet of paper. A cardboard template the size of the negative may be used.

Note: Avoid watermark area of paper. Handle only by the edges to avoid transfer of moisture or dirt from fingers to image area (including on the reverse).

### D. Sensitization solution preparation:

Note: The total volume of sensitizer needed depends on the negative size, the type of paper, and absolute humidity. There should be enough sensitizer to make 3-5 passes with the coating rod.

- 1) Prepare a 1:1 mixture of solution A (Ferric ammonium citrate) and solution B (Potassium ferricyanide) in a 10 ml beaker. Use a separate syringe (no needle) for each solution (label them).

Use the following as a starting point:

- solution A (Ferric ammonium citrate) 0.2 ml
- solution B (Potassium ferricyanide) 0.2 ml

- 2) Use a third syringe to mix the solution thoroughly by passing the liquid in and out of a syringe two or three times. Use this syringe to transfer the sensitizer solution to the paper.

### E. Transfer of the sensitizer solution to the paper:

Note: Coating should be done at a room temperature of between 18 and 22 °C and a relative humidity of around 75%. (If conditions are too cold or dry, surface crystallization will occur, and too high an ambient temperature or relative humidity may cause the solutions to penetrate too deeply into the paper).

- 1) Tape the marked paper onto a sheet of glass and clean the paper surface with a blower.
- 2) Arrange glass coating rod (it must be free of dust and grease), blotting paper, and loaded syringe nearby.
- 3) Gently eject solution from the syringe along the top of the coating area. Place the glass rod spreader on the paper just above the liquid line. Draw the rod into the solution, pause briefly (about a second), allowing the fluid to distribute itself evenly along the length of the rod. Then smoothly pull the spreader down the length of the area to be coated. Coat 1-2 cm beyond the image area.

The surface may look blotchy at this stage, but it will even out in the next few moments. One 'pass' for a 10x15 cm area will take about 3 to 5 seconds. Apply only a slight pressure, otherwise the paper surface will be abraded. At the bottom of the first pass, 'hop' the spreader over the line of solution and smoothly push it back up to the top of the sheet, thus repeating the process, but in the opposite direction.

Make 3 to 5 passes over the paper in this way. It is best to stop before all the solution has been absorbed into the paper. Soak up the excess solution with a strip of blotting paper. (Alternatively a brush maybe used to apply the solution).

5. Remove the paper from the sheet of glass. Place the coated paper in the oven for 5-10 minutes. Ideally the temperature should be between 35-40 °C (95-105 F). Allowing the dried paper to "rest" for half an hour or more may improve image quality. Unlike other Fe, Pt, and Pd processes cyanotypes are relatively unaffected by relative humidity.

### **III. Image formation:**

- 1) Place the dried paper in contact with the negative (sensitized surface to emulsion) in a contact printing frame. This can be made from a clipboard, piece of art foam, piece of glass and rubber bands. Alternatively, a purchased contact printing frame which permits opening halfway to check the image without disturbing the registration of the print and negative may be used.
- 2) Expose to UV light source. Printing times will vary according to negative density. The image is partially formed during the exposure. A commercial contact printing frame permits examination the print by opening one half without disturbing the registration of the negative to the print. This 'inspection' must be carried out in an area shielded from the UV source, otherwise the print will be fogged.

**Caution:** To prevent eye damage, do not look into UV sources.

Note: the UV light source may be the sun, a sunlamp or a specially designed UV source (or even a tanning bed if you wish to do large images).

- 3) Clear print in a water bath for about 1 minute. Wash in running water for 5-10 minutes, or until highlight (white) areas in print have cleared.
- 4) Hang to dry.

#### IV. Data summary - a useful practice to maximize image quality

Print #	
Paper type	
ml solution A	
ml solution B	
# of passes for coating	
Room temperature	
Sizing	
Exposure time	
Rinsing time	
Drying conditions	

Print #	
Paper type	
ml solution A	
ml solution B	
# of passes for coating	
Room temperature	
Sizing	
Exposure time	
Rinsing time	
Drying conditions	

#### References

Crawford, William. *The Keepers of Light*. p.163-165, 177-180

Reeve, Catharine and Sward, Marilyn. *The New Photography*. p 55-63.

Ware, Mike. *Cyanotype: The History, Science and Art of Photographic Printing in Prussian Blue*. Science Museum and National Museum of Photography, Film and Television. England: Cromwell Press. 1999.