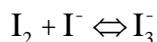


## Determination of the Stability Constant of the Tri-Iodide Ion by Solvent Extraction

### Introduction

Molecular iodine reacts with iodide to form a complex, called the tri-iodide ion, according to the reaction:



The stability constant of this ion,  $K_{st}$ , is calculated from:

$$K_{st} = \frac{[I_3^-]}{[I_2][I^-]}$$

While there are many ways to experimentally determine this constant, this experiment is designed to use distribution equilibria. Iodine has very low solubility in water (0.0162 g/100 mL @ 0 °C) but dissolves readily in nonpolar solvents such as carbon tetrachloride and hexane.

In this experiment, iodine is distributed between aqueous and hexane phases. This distribution is shown schematically below (Figure 1). The distribution coefficient,  $K_D$ , is calculated using:

$$K_D = \frac{[I_2]_{Hexane}}{[I_2]_{Aqueous}}$$

The distribution ratio,  $D$ , for this system is calculated using:

$$D = \frac{[I_2]_{Hexane}}{[I_2]_{Aqueous} + [I_3^-]_{Aqueous}}$$

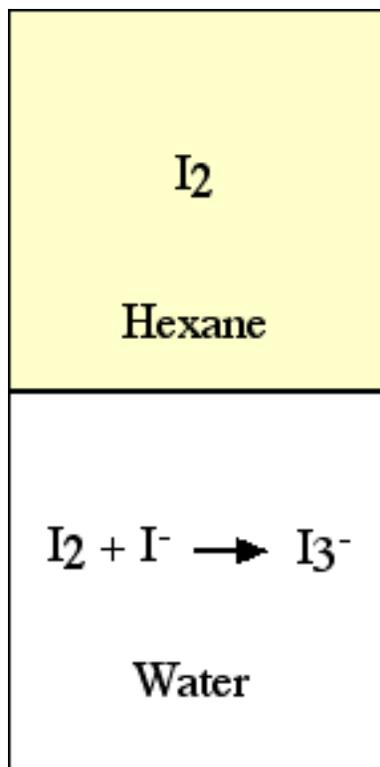


Figure 1. Distribution of iodine between aqueous and hexane solutions.

Substituting the stability constant expression into the distribution ratio expression and solving for  $D$  yields the following expression:

$$D = \frac{K_D}{1 + K_{st} [I^-]}$$

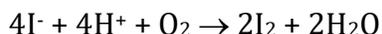
This is the equation used to determine  $K_{st}$ . The value for  $K_D$  is 35.

After equilibrium has been achieved, the iodine in each liquid phase is determined by an oxidation-reduction titration using standard sodium thiosulfate as the titrant. Sodium thiosulfate is used almost exclusively to titrate iodine according to the reaction:



From the known concentration of thiosulfate, and the volumes of thiosulfate and iodine titrant, the concentration of iodine is readily calculated.

This titration must be carried out in weakly acidic solution (pH ~ 5), because in neutral or alkaline solution the thiosulfate is partially oxidized by iodine to tetrathionate and sulfate. In strongly acidic solutions the thiosulfate decomposes to sulfur and sulfite ion. Iodine has a high vapor pressure, so care should be taken to prevent its loss. Erlenmeyer flasks should be used for the titration and moderate mixing conducted by swirling the contents of the flasks. Flasks should remain stoppered until titrated. At room temperature volatilization losses are negligible if the solution contains at least 4% potassium iodide. In acid solution, the iodide will be oxidized to iodine by oxygen from the air according to the reaction:



The rate of this oxidation reaction increases with decreasing pH and increasing intensity of sunlight striking the flask.

Aqueous iodine solutions appear yellow to brown; this color becomes paler as the concentration of iodine decreases. One drop of 0.1N I<sub>2</sub> will turn 100 mL of deionized water pale yellow. While it is feasible to use iodine as its own indicator in titrations with thiosulfate, a much more dramatic endpoint is observed when starch solution is added as an indicator.

Iodine reacts with amylose to form an intense, deep blue color. As low as 1 x 10<sup>-5</sup> M iodine can be detected by 0.2% amylose in 100 mL of water containing potassium iodide. Potato starch (20% amylose and 80% amylopectin) is normally used as the indicator in iodine titrations. This starch solution is added just before the endpoint is reached. When the pale yellow iodine color begins to fade, the starch solution is added, and the titration continued until the endpoint is reached.

Solutions needed for this experiment:

Solutions prepared by the student	Solutions provided by the instructor
Iodine solution	Starch Indicator Solution
0.0100 M sodium thiosulfate	0.100 M sodium thiosulfate
0.1 M hydrochloric acid	12 M hydrochloric acid
0.1 M potassium iodide	

Specialized equipment needed:

In this experiment, you will be using a 250 mL separatory funnel (Figure 2).

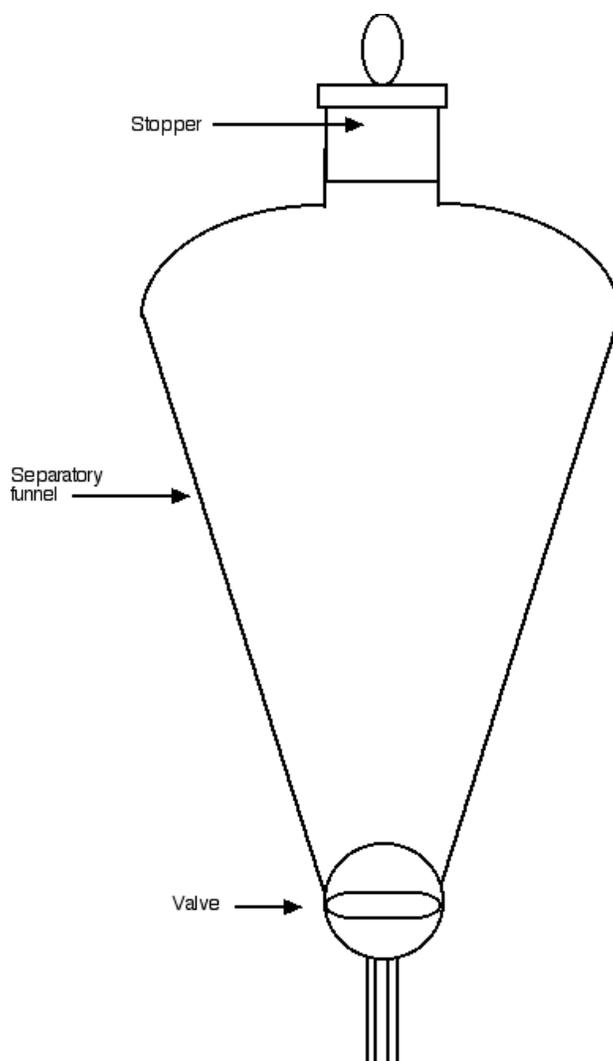


Figure 2. Typical separatory funnel.

### Preparation of Iodine solution

1. Using the top loading balance, weigh approximately 5.00 g of reagent grade potassium iodide. ***Make sure to record the exact weight of potassium iodide, to two decimal places, in your notebook.*** Dissolve the potassium iodide in approximately 25 mL of DI water.
2. Weigh approximately 1.00 g of iodine, record the exact weight of iodine, to two decimal places, in your notebook, and add the iodine to the potassium iodide solution. **(NOTE: do NOT weigh the iodine in the analytical balance!!)**
3. Stir the solution carefully to dissolve all of the iodine. (Iodine dissolves slowly, so this step may take some time.) When all of the iodine has dissolved, analytically transfer the solution to a 250.00 mL volumetric flask and QS with DI water.
4. Clean a brown glass bottle with soap and water, rinse 2-3 times with small portions of DI water, followed by 2-3 rinsing's with small portions of your iodine titrant. After rinsing the brown bottle with iodine solution, store the rest of your iodine solution in the brown bottle. Label the bottle with your name (or initials) and date. This solution is stable for a long time, provided it is stored in a dark place (like your locker). All waste materials from this step may be flushed down the sink with water.

### Experimental Procedure

1. Using a graduated cylinder, measure 75 mL of the iodine solution and transfer this solution to the separatory funnel.
2. Add 75 mL of hexane to the separatory funnel, stopper the funnel, and shake the solutions 3-5 times. Invert the funnel  $\sim 45^\circ$ , and open the valve to vent the separatory funnel (see Figure 3 below). **BE CAREFUL THAT YOU DO NOT POINT THE FUNNEL AT YOURSELF OR ANOTHER STUDENT!!**

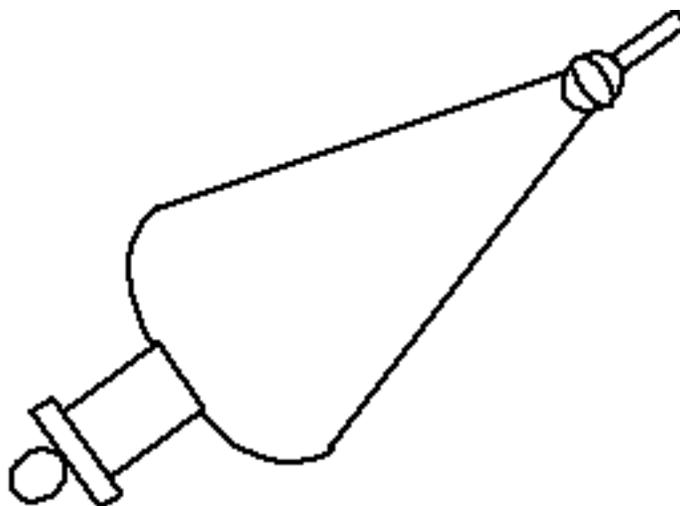


Figure 3. Correct orientation for venting of separatory funnel.

It is extremely important that the funnel is vented. If not properly vented, the funnel could shatter explosively from the increasing pressure of hexane vapor. Even if the funnel does not shatter, it may spurt hexane and water solutions all over the laboratory.

Repeat the process of shaking and venting until only a minimum amount of hexane vapor is released. Set the funnel upright, in a ring stand, and allow the aqueous and hexane layers to separate (Figure 4).

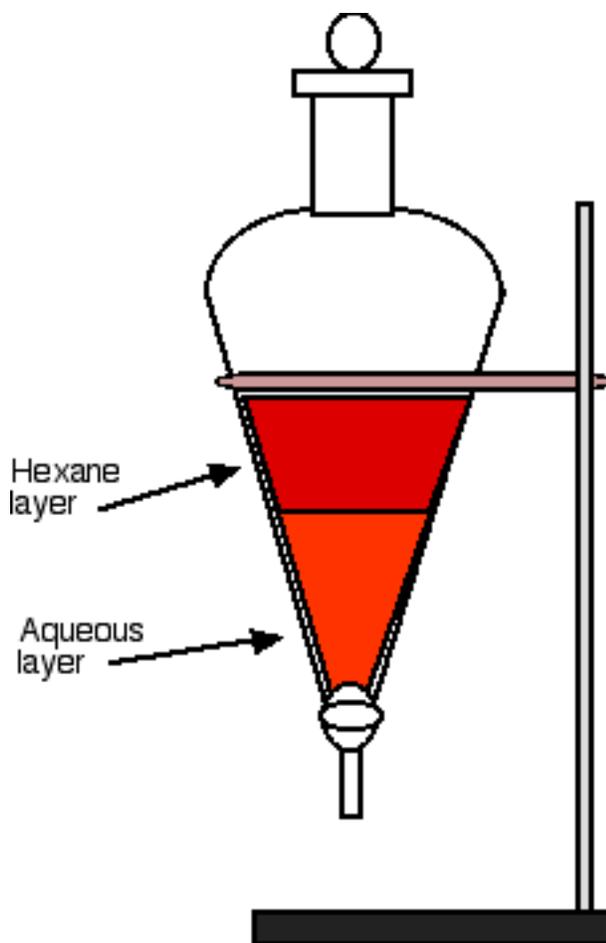


Figure 4. Hexane and aqueous layers after separation. Colors may vary.

3. Carefully transfer the aqueous layer to a clean Erlenmeyer flask. Do NOT allow any hexane to get into the aqueous layer. Stopper and label this flask.
4. Carefully transfer the hexane layer to a clean Erlenmeyer flask. Do NOT allow any aqueous phase to get into the hexane layer. Stopper and label this flask.
5. Now that the hexane and aqueous layers have been separated and isolated from each other, the two layers can be titrated to determine their respective iodine concentrations.

#### Titration of hexane layer:

1. Carefully fill your burette with the hexane solution. Measure two 30.00 mL aliquots of the hexane solution into two different clean 250-mL Erlenmeyer flasks. It isn't important for you to dispense exactly 30.00 mL – it IS important for you to know the volume of hexane exactly (to two decimal places). Stopper these flasks until you are ready to titrate them.
2. Clean the burette with soap and water, rinse with tap water, and then rinse with 2 or 3 small portions of 0.01000 N sodium thiosulfate solution, prepared by volumetric dilution of the 0.1000 N sodium thiosulfate provided. Then fill the burette with 0.01000 N sodium thiosulfate solution and record the initial volume to two decimal places.
3. Add 15 mL of 0.1 M potassium iodide solution to the first hexane aliquot. Add one or two drops of 0.1M HCl to the flask. Swirl the flask to extract some of the iodine from the hexane layer into the aqueous layer. Titrate the contents with sodium thiosulfate, occasionally swirling the flask to extract more iodine from the hexane layer into the aqueous layer. As the titration proceeds, you will notice the color of the hexane layer fading, while the aqueous layer becomes yellow. When the hexane layer is pale purple and the aqueous layer is yellow or colorless, add 2 mL of starch indicator solution. The aqueous layer will become dark blue. Continue titrating, with swirling, until both layers are colorless. Record the final volume of sodium thiosulfate used, measuring this volume to two decimal places.
4. Refill the burette with sodium thiosulfate solution, if necessary, and record the initial volume. Repeat the titration procedure on the second 30 mL aliquot of hexane solution.

#### Titration of aqueous layer:

1. Using 10.00 mL transfer pipettes, transfer two 10.00 mL aliquots of the aqueous phase into separate Erlenmeyer flasks. Add one or two drops of 0.1M hydrochloric acid to each flask.
2. Titrate each aliquot with standard 0.01000 N sodium thiosulfate solution until a light yellow color develops. Once the solution becomes light yellow, add 2 mL of starch indicator solution. The color will become blue.
3. Continue titrating until the solution becomes colorless. Record the final volume of sodium thiosulfate solution used, and repeat the titration on the second aqueous aliquot.

When you have completed your titrations, you should have the following data recorded in your notebook.

Aqueous data:	1 <sup>st</sup>	2 <sup>nd</sup>	Average
Vol. aqueous Iodine solution, mL	10.00	10.00	
Normality, sodium thiosulfate	0.01000 N	0.01000 N	
Vol. thiosulfate, mL	24.50	24.75	
Concentration iodine	12.25 mM	12.38 mM	12.32 mM

Hexane data:	1 <sup>st</sup>	2 <sup>nd</sup>	Average
Vol. Hexane Iodine solution, mL	30.00	30.00	
Normality, sodium thiosulfate	0.01000 N	0.01000 N	
Vol. thiosulfate, mL	39.50	39.55	
Concentration iodine	6.59 mM	6.59 mM	6.59 mM

$K_D = 35$  (use this value for all further calculations)

$$D = 6.59 \text{ mM} / 12.32 \text{ mM} = 0.535$$

$$D = \frac{K_D}{1 + K_{st} [I^-]}$$

$[I^-]$  is unique for each student, and depends on the mass of potassium iodide used in making the iodine solution. Substitution of the molar concentration of iodide into the above equation allows calculation of  $K_{st}$ .

Lab report.

A sample report is included at the end of this procedure.

**WASTE DISPOSAL:** All hexane wastes must be disposed of in the proper organic waste container. Your instructor will show you where this container is located. All aqueous wastes can be poured down the sink.

SAMPLE REPORT

Stability Constant of Tri-Iodide Ion  
Matt Damon

Aqueous data:	1 <sup>st</sup>	2 <sup>nd</sup>	Average
Vol. aqueous Iodine solution, mL	10.00	10.00	
Normality, sodium thiosulfate	0.01000 N	0.01000 N	
Vol. thiosulfate, mL	24.50	24.75	
Concentration iodine	12.25 mM	12.38 mM	12.32 mM

Hexane data:	1 <sup>st</sup>	2 <sup>nd</sup>	Average
Vol. Hexane Iodine solution, mL	30.00	30.00	
Normality, sodium thiosulfate	0.01000 N	0.01000 N	
Vol. thiosulfate, mL	39.50	39.55	
Concentration iodine	6.59 mM	6.59 mM	6.59 mM

$$K_D = 35 \text{ (given in preparation)}$$

$$D = 6.59 \text{ mM} / 12.32 \text{ mM} = 0.535$$

$$D = \frac{K_D}{1 + K_{st} [I^-]}$$

$$[I^-] \text{ from iodine titrant} = 0.215 \text{ M.}$$

$$K_{st} = 299$$