

Henry's Law Constant and Free Energy of Solvation of 1,1,1-Trichloroethane

Rarely are journal articles sufficiently complete enough that a newcomer to the laboratory can easily repeat the experiment. However, G.A Robbins, S. Wang, and J. D. Stuart's article "Using the Static Headspace Method to Determine Henry's Law Constants" is nicely written and contains complete detail for the procedure¹. Please read this article. Use this article to design a procedure to prepare the samples to determine the Henry's Law constant for 1,1,1-trichloroethane in water. We won't do the temperature dependent part described in the article. Also, we only use one solute to avoid confusion. After forming the head space allow about 30 minutes for equilibration. Later in the semester we will do a computational lab to calculate this same result.

We will use our Varian Gas Chromatograph/Mass Spectrograph, GC/MS, for the analysis. Since we are only analyzing one compound, a GC/MS isn't necessary. In fact the GC/MS is a vast overkill. But, the excellent sensitivity of this instrument will make this experiment easier to do. You can also check the mass spectrum of the peak in the run to make sure it matches the library spectrum of 1,1,1-trichloroethane. Otherwise, we will just use the instrument in its GC mode, the analysis of the mass spectrum is not necessary. The GC type output of the instrument is called the Total Ion Chromatogram, or TIC. The TIC is the sum off all of the signals for all the mass fragments of your compound. The TIC is comparable to the output of a flame ionization detector, FID, in conventional GC work.

We choose a solvent delay to allow the air, methanol, and water vapor that we inject to pass through the mass detector before turning on the source. Turning on the source just before the peak of interest increases the life-time of the source filament and helps to avoid confusion of the analyte peak with the peak for the air, methanol, and water vapor.

Sample Preparation

Use the Stuart article to prepare your samples. Run at least five samples. You can use intermediate headspace volumes to those given in the article or repeat some values.

GC/MS settings:

1. The "Henry03.mth" method contains all the settings necessary to run this experiment: You should not change the settings in this method.

GC Temperature Zones:

Injector 150°C, Oven 50°C, Transfer line 200°C.

Mass Spectrum settings:

solvent delay 1.75 min; scan range 40-300 m/e; sampling rate 1 per sec;
run time 3 min.

GC Injector settings:

Split mode, 5:1 split ratio for very high sensitivity (split ratios of 200:1 are much more common)

Report

Report the Henry's Law constant and the uncertainty propagated from the uncertainty of the slope and intercept. Compare your result to the literature value. Calculate the Gibbs Free Energy

of solvation for your sample, including the uncertainty propagated from the uncertainty in the Henry's Law constant.

Ground water geologists and engineers often express aqueous solubilities in mg/L, which is equivalent to ppm. Convert your dimensionless Henry's Law constant to H_p using eq. 7 in Stuart. Assuming the density of the solution is that of water, 0.99821 g/mL, the aqueous solubility in mg/L can then be calculated at 20.0°C from:

$$H_p = K_{PX} = \frac{P_i}{X_i} = \left(\frac{VP M}{s} \right) 72.91 \frac{\text{mg mol atm}}{\text{g L torr}}$$

where VP is the partial vapor pressure in torr, M is the molar mass of the solute in g/mol, s is the solubility in mg/L (or ppm). For example, the Henry's Law constant for O₂ at 25°C is $H_p = K_{PX} = 4.34 \times 10^4$ atm, giving the concentration of O₂ in water in equilibrium with air of about 8 ppm. Use this equation to calculate the aqueous solubility of your compound assuming a vapor pressure of 1 torr. Derive this equation in your report to give you practice in converting concentration measures and equilibrium constants.

Discuss the relationship of the Gibbs Free Energy of solvation to the octanol-water partition coefficient. What additional experiment would you need to do using this Henry's Law technique to calculate the octanol-water partition coefficient? Discuss the chemical significance of this experiment. For example, who would need to know this information?

Varian 3800/2000 GC/MS Operating Instructions: Head Space Analysis

General Notes:

- * All mouse functions are accomplished with the left button unless specified.
- * The function of each icon can be listed by placing the cursor over the icon and waiting a second or two. The icon label will be listed on the screen.
- * Don't use the go-away box on the 3800.44 or 2000.40 control windows. Minimize them instead.
- * Do use the go-away box for the Review/Process Data- SatView window.

Procedure:

PREPARATION

1. Check that the helium pressure gauge on the wall reads 40-80 psi.
2. On the computer, note the Varian Star Toolbar. This is a wide toolbar that runs down the left side of the screen. If the Varian Star toolbar runs across the bottom of the screen, click on the background of the toolbar and drag it to the left. Click on the System Control icon. This icon is at the top.
3. Pull down the Windows menu and select 3800.44 to display the GC control panel.
4. To select the desired method, click on the "Activate a Method" icon. This icon is an "open file folder" icon in the middle of the top icon bar, just to the right of the method pull down list. Find the folder for CH341; you may need to go up a level. In this folder, the method "Henry03.mth" is designed for this experiment. Click Open to continue.
5. Check the GC temperature zones, which are listed in the middle of the screen. The column oven should be 50°C, the front injector 150°C, and the middle injector 60°C. We will use the front injector for this lab. The total run time is 3 min. Check for the total run time, which is listed as the "End Time." Note the two status indicator lights: the Equilibrating/Ready light and the Fault/No Fault lights should both be green before beginning a run. These status indicators are in the upper left-hand block of the control window.
6. Minimize the 3800 control window.
7. Pull down the Windows menu and select 2000.40 to display the MS control panel.
8. Click on the Auto Tune button.
9. The tuning procedure calibrates the mass axis. Choose the "FC-43 mass calibration" tuning

mode in the pull-down list box in the middle of the window. Make sure the check box to the left of the pull-down list box is checked, and the other three check boxes are cleared. Click on Start Auto Tune. The system will open the calibration valve on the MS. This valve allows the vapor from a fluorinated organic liquid, FC-43, to enter the MS. The text box across the bottom the screen shows the progress of the Auto Tune procedure. After the procedure is complete, check to see that "Multipoint mass cal: completed" has been printed in the text box.

10. Click on the Acquisition button, at the far right of the MS control window.

RUNNING A SAMPLE

1. The status indicators should both be green and be labeled Ready and No Faults.
2. The system is ready to begin. The start of data acquisition is signaled by the mechanical switch on the top of the injection port. When you press down on this switch with the syringe, data acquisition will begin.
3. Remember to use only a blunt tipped, conical needle syringe, to avoid destroying the Merlin GC inlet. The syringe for this experiment should be fitted with a sampling valve. The syringe is open when the knurled barrel of the valve is pushed towards the base of the syringe. The syringe should be clean and ready to use. However, flush the syringe at least 50 times with air to remove traces of cleaning solvent.
4. We next need to set the data directory and file name as follows. Pull down the Inject menu and choose Inject Single Sample... Click on OK in the next dialog box. Click the Data Files button and navigate to the folder C:\saturnws\ch341\data. Next enter a file name in the Data File names box in the upper right-hand corner of the Data File Generation window. The data file name should end with a "%i" so that the program will place the injection number after each successive file name. For example, you might use your initials: "tws%i". Click OK. In the Inject Single Sample window use the default settings: Sample name-Default Sample, Sample type-Analysis, Inj.-1. For the "Inject the sample using the method:", c:\SaturnWS\ch341\Henry03.mth should also already be set. Click on Inject.
5. In the Saturn 2000 control window, the yellow "waiting.." prompt should be blinking in the menu bar. Doing an injection will now automatically start the data acquisition. After the data acquisition period, the data will be transferred to the SatView analysis application and the integral will be calculated.
6. **Head Space Analysis:** Flush out the syringe with your sample vapor at least three times. Keep your samples at 25°C in the constant temperature bath while you take your sample. Inject 250 uL with a gas tight syringe fitted with a syringe valve. Fill the syringe slowly, counting to 20 to make sure you fill at the same rate each time. Since you are using a valved syringe, there is no hurry between taking the head-space sample and injecting the sample in the GC. Inject your sample by pushing the syringe needle into the injection port on the top of the GC. Be sure to push straight down and guide the needle in as it is very fragile and easily bent. When the valve is

pushed into the open position against the injection port, then and only then push the barrel of the syringe to inject the sample. Remove the syringe immediately after injection.

7. Note the data file name. This name will be listed in the upper-right corner of the acquisition dialog window.
8. To view the data while it is being taken, click on the Hide Keypad button, which is on the left side in the middle of the control window. Pull down the adjacent list box and select Spectrum and Chromatogram. Both the yellow Spectrum and Chromatogram windows should be displayed. The relative heights of these windows can be adjusted by dragging the border between the two windows up and down. (Sometimes, this border is left too low so that only one window shows, even though you have chosen to display "Spectrum and Chromatogram." If this happens, move the mouse to the bottom of the yellow window until the cursor changes to "=". You can then drag the border up to reveal the second yellow window.)
9. After the solvent delay has passed, you will see the Total Ion Chromatogram accumulating on the screen. While it is running, you may adjust the graph parameters, including the vertical scaling using the slider at the far right of each yellow window. Most often though, you should just click on the Auto-scale button. The Auto-scale button looks like a chromatographic peak with a double box around it. This button is in the button bar above the chromatogram window and is the left-most button in the middle button group. If you need to stop the run while it is in progress, click on the Show Keypad button, and then select Reset. To end early you will also need to reset the GC. Pull down the Windows menu and choose 3800.40, and again click on Reset, and finally minimize the GC control window to return to MS data acquisition.
10. You can display information about the current MS scan by clicking the Scan Information icon. This icon looks like a small piece of white paper with tiny lettering. Clicking again hides this information box. You can display the current cursor m/z position and the corresponding data value by selecting the Cursor Display icon. This icon looks like a small mass spectrum with one red peak. Clicking again hides this information box.

Data Analysis

11. When the chromatographic peak returns to baseline or the run is completed, you can display the data in the Review/Process MS Data window. To open your data in the Review/Process MS window click on the small black icon that has a representation of the chromatogram in yellow and green. This small icon is in the middle of the screen above the yellow chromatogram window. (There are two other larger icons on the screen with the same symbol. These larger icons are used to enter the Review/Process MS Data application with a previously saved data file.)
12. In the SatView application window, pull down the Spectra menu and make sure that "Background Correct Spectra" is not checked. If it is checked selecting that entry will clear this mode.
13. Move the cursor over the chromatogram trace. Clicking the mouse will load the mass spectrum that was taken at that time into the window, on the top. Individual mass spectra or

several consecutive spectra that have been averaged can be displayed. Pull down the Spectra menu, slide right on Spectrum Averaging and choose Single spectra. Click on the chromatogram trace to load single spectra for viewing. Now return to the Spectra menu, slide right on Spectrum Averaging and choose 5 point spectrum. Now clicking on the chromatogram trace will display the averaged result of 5 spectra centered on the time that you selected.

14. Areas of either the chromatogram or mass spectrum can be enlarged by highlighting a box around the area by holding the left mouse button down and dragging around the area. Clicking the red A icon, above the spectrum window, will return to the full X and Y expansion.

15. To prepare for printing, press the right mouse button with the mouse in the mass spectrum window and slide right on Options. If you want a listing of the ion fragments and their abundances, make sure “print ions and intensities” is checked. Normally, we don’t need a listing and “print ions and intensities” should not be checked. To print the mass spectrum, click right again and choose “Print Spectrum.” In the print preview screen, click on the “print page” icon. This icon looks like a printer with a single sheet of paper. Click on the “Exit!” menu item to return to the data viewer.

16. To find the area of the peak, pull down the Quantitation menu and choose Review Results of the Active File. The area will be listed in the peak table. You can see the integration process by clicking on View; click on Done from the View window. Click on Done from the Quantitation window to return to the main MultiChrom window. When you are finished with data analysis, click the go-away box on the MultiChrom window and the SatView window.

17. You should now see the 2000.40 MS acquisition window. If necessary, click on the Show Keypad button to see the acquisition controls. Check the status indicators. If they are both green, the system is ready for the next sample. The next injection will increment the injection number in the data file name (i.e. you don't repeat step 9 in the PREPARATION section).

18. Flush out the syringe with air at least 20 times to remove traces of the sample.

SHUT DOWN PROCEDURE

1. Minimize the 2000.44 acquisition control window.
2. Maximize the 3800.44 control window, or alternatively pull down the Windows menu and choose 3800.44.
3. Click on the Activate a Method icon. (This icon is an “open file folder” icon in the middle of the top icon bar.) If you are in the CH341 folder; you will need to go up a level. Select the “standby” method. Click Open to continue. The standby method sets the oven at 50°C, the front injector at 200°C, and the middle injector to 50°C. The split vents are turned off to conserve on helium.
4. Flush out a syringe with methylene chloride or methanol. Be sure to eject the cleaning solvent

into a waste container. Do not eject back into the source bottle as it will contaminate the entire bottle.

Reference

1. G.A Robbins, S. Wang, and J. D. Stuart, "Using the Static Headspace Method to Determine Henry's Law Constants," *Anal. Chem.*, **1993**, *65*, 3113-3118