

Experiment 4. Binary Liquid-Vapor Phase Diagram

Adapted from Shoemaker *et al.* Experiment 14 (page 207)

1 Introduction

This experiment is concerned with the heterogeneous equilibrium between two phases in a system of two components. The particular system to be studied is the Acetone-Chloroform mixture at a pressure of 1 atmosphere. This system exhibits a strong deviation from Raoult's law in the form of a maximum boiling point.

2 Theory

For a detailed discussion of the theory behind this experiment see the theory section for Experiment 14 of the book on p. 207. You will need to read this section in order to understand how to determine Molecular weights.

3 Experimental procedure for acetone-chloroform system

Chloroform is a suspected carcinogen. Use gloves and handle the solvents with care.
CAUTION: The ORGANIC LIQUIDS are TOXIC and FLAMMABLE! Use all necessary precautions to avoid accidents!
CAUTION: DISPOSE OF THESE ORGANIC LIQUIDS by placing in the Waste Containers provided. DO NOT POUR DOWN THE DRAIN!

You will have to assemble the distillation apparatus according to the illustration on page 212 of the text

It is very important that the glassware is not rinsed with H₂O!

Show your TA or lab coordinator the distillation apparatus before commencing.

Ask your TA for instructions on how to use the refractometer.

- o Place condensed vapor (distillate) samples taken from the condenser into vials labeled with V.
- o Place liquid (residue) samples taken from the distillation flask into vials labeled with L.

The samples of residue and distillate are analyzed, and their compositions are plotted on a boiling-point diagram against the temperatures at which they were taken. Take samples of about 2 mL in size. In the case of distillate, the temperature to be plotted for each sample should be an average of the initial and final values during the taking of the sample. In the case of the residue, the temperature to be plotted should be that recorded at the point where the distillation is stopped to take the



sample of residue. Do not use the temperatures from the instructions below for plotting; these are only approximate temperatures at which you should collect the samples. After the samples are collected, their refractive indices must be measured and recorded. This can be done at any convenient time.

- Put 90 ml of acetone into the distillation flask. Determine its boiling point by carrying out the distillation until a constant temperature is obtained, should be near 55°C. Collect sample 1V from the condenser when the distillation is proceeding at a normal (not excessive) rate at about the desired temperature, quickly replace the receiver with a vial and read the thermometer. After about 2 mL has been collected, read the thermometer again, replace the receiver, and seal the vial tightly. The temperature to be plotted should be an average of the initial and final values during the taking of the sample. Turn off and lower the heating mantle to halt the distillation. When the temperature just begins to fall take another thermometer reading. Collect sample 1L after the flask cooled about 15 °C. Remove the glass plug on the side arm of the flask and pipet about 2 mL of sample into the appropriate vial, and stopper the vial. In the case of the residue, the temperature to be plotted should be that recorded at the point where the distillation was stopped. Collect the samples and record the temperatures of the subsequent V and L samples in a similar manner.
- Return the distillate from step 1 into the distillation flask. Add 10 ml of chloroform and start distillation. When the temperature reaches about 58°C, collect samples 2V and 2L.
- Resume the distillation procedure. Collect samples 3V and 3L at around 60°C.
- Resume the distillation procedure and continue to about 61°C. Remove heating and then add 17.5 ml chloroform and 32.5 ml acetone. Collect samples 4V and 4L at around 62°C.
- Resume the distillation procedure and continue to about 63°C. Remove heating and then add 25 mL chloroform and 25 mL acetone. Resume distillation. Collect samples 5V and 5L at around 63.5°C.
- Resume distillation, continue until the boiling point ceases to change significantly (at around 64.5°C), then collect samples 6V and 6L at around 64.5°C.
- Discard the distillate.
- Rinse the distillation flask with a little chloroform. Then put 40 ml chloroform into the flask, collect samples 7V and 7L at around 61°C.
- Return the distillate from step 9 into the distillation flask. Add 4 ml of acetone.
- Resume distillation and collect samples 8V and 8L at around 62.5°C.
- Return the distillate of step 11, and then add 5 mL of acetone.
- Resume distillation and collect samples 9V and 9L at around 63.5°C.
- Resume distillation and collect sample 10V and 10L at around 64.5°C.
- After the samples are collected, their refractive indices must be measured and recorded. This can be done at any convenient time.

	1L	2L	3L	4L	5L	6L	7L	8L	9L	10L
n_D										
	1V	2V	3V	4V	5V	6V	7V	8V	9V	10V
n_D										

Calibration function

Prepare calibration mixtures of acetone (A) and chloroform (B) with mole fraction of chloroform, $x_B \approx 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85,$ and 0.95 , by weighing calculated amounts of the two components. If you prefer working with volumes you can convert the mass of chloroform needed to prepare 5 mL of mixture with the desired mole fraction of chloroform into volume of chloroform. Using the density of chloroform 1.492 g/mL and the density of acetone 0.791g/mL you will need 0.27 mL of chloroform diluted with acetone to 5.00 mL to prepare solution with 0.05 mole fraction of

chloroform. The remaining solutions with $x_B \approx 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85,$ and 0.95 can be prepared using 0.81, 1.33, 1.85, 2.36, 2.86, 3.35, 3.83, 4.30, and 4.77 mL of chloroform, respectively, and diluting to 5.00 mL with acetone. You must record the individual masses or volumes of the components accurately in order to compute the mole fractions. Calculate the composition of these mixtures. Measure the refractive indices of the mixtures using an Abbe refractometer. Also measure the refractive indices of the pure components acetone and chloroform.

Mass _{chloroform} or Vol _{chloroform}									
Mass _{acetone} or Vol _{acetone}									
$x_{\text{chloroform}}$	0.15	0.25	0.35	0.45	0.55	0.65	0.75	0.85	0.95

Data Analysis

- 1) Enter the weights of acetone and chloroform used in each calibration mixture into a spreadsheet. Calculate the mole fraction x_{CHCl_3} of chloroform in each of the calibration mixtures. Also enter the respective refractive index values (n). Create a graph of x_{CHCl_3} versus n . Fit the data to a second order polynomial and express x_{CHCl_3} as a function of n . This function will be used to convert the refractive indices of the chloroform-acetone mixtures to mol fractions of chloroform x_{CHCl_3} .
- 2) Using the calibration function calculate the composition of residues (1L–10L) and distillates (1V–10V) from their refractive indices. Express the sample composition in terms of mole fraction of CHCl_3 x_{CHCl_3} .
- 3) Tabulate the mole fraction of CH_3Cl , x_{CHCl_3} in the distillates (1V-10V), and the boiling point temperatures at which you collected the vapor samples. Sort the table in the order of increasing mole fraction of CH_3Cl , x_{CHCl_3} .
- 4) Tabulate the mole fraction of CH_3Cl , x_{CHCl_3} in the residues (1L-10L), and the boiling point temperatures at which you collected the vapor samples. Sort the table in the order of increasing mole fraction of CH_3Cl , x_{CHCl_3} .
- 5) Construct the T - X phase diagram by plotting the boiling points (y-axis) against the liquid-phase (1L–10L) mole fraction of

CH_3Cl , x_{CHCl_3} (x-axis) and superimposing on the same graph a plot of the boiling points versus the equilibrium vapor-phase (1V–10V) mole fraction of CH_3Cl , x_{CHCl_3} .

- 6) Label all fields of the diagram to indicate what phases are present. Report the azeotropic composition and temperature, together with the atmospheric pressure (i.e., the properly corrected barometer reading).