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| Liquid-Vapor Equilibrium of Chloroform and Acetone |
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# Abstract

This experiment seeks to determine the relationship between the liquid and vapor phases of a binary solution of chloroform and acetone at different ratios of concentration. This was done by distilling binary solutions of chloroform and acetone in different concentrations and measuring the mole fraction of the distillates and residues, along with recording the boiling point of the binary mixtures. At about 21% mole fraction acetone and a boiling point of 336 K, the boiling point reached a maximum and the residue and distillate mole fractions were very similar. Thus, it was concluded that a negative azeotrope exists in this solution at 21% mole fraction acetone.

# Introduction

When a binary solution, a solution of two liquids, boils, they may boil in different ratios to their mole fractions in solution due to differing vapor pressures and azeotropic interactions in their solutions. In these binary solutions, the more volatile component will tend to be richer in concentration in the vapor compared to the liquid, unless the solution reaches an azeotropic point during boiling. In this azeotropic point, the concentrations of the mixture between the liquid and vapor phase do not change, and they usually constitute a minimum or maximum boiling point of the binary solution.

To test this behavior, distillation can be used to compare the mole fractions between the distillate and residue of a binary solution. The residue will act as the original binary solution, with a known mole fraction. The distillate will be the product of the vapors boiling off in different concentrations and can be collected in the liquid form. To determine the mole fraction of this binary solution of unknown concentration, a calibration curve can be first determined using the refractive index of different concentrations of the binary solution.

As the refractive index of a solution is linear to the mole fraction of the components of the binary solution, measuring the refractive index of known binary mixtures will allow for the creation of a calibration curve comparing refractive index to mole fraction. Using this calibration curve will allow the estimation of a mole fraction from the collected distillates and residues and plotting these on a graph with their associated boiling points will create a temperature-composition diagram. From this diagram, azeotropic behavior and identification can be evaluated.

# Experimental

To begin this experiment, six calibration solutions of acetone and chloroform were prepared, with 5, 4, 3, 2, 1, and 0 mL of acetone, respectively, and enough chloroform to make each solution 5 mL total. Then, the refractive index of each solution was measured with a refractometer. Using the refractive index and the known mole fraction of each calibration solution, a calibration curve was calculated.

The next part of the experiment was the distillation of binary solutions. First, 50 mL of acetone was added to a distillation flask and was distilled. During distillation, 2 mL samples of the distillate and residue were removed, and the refractive index of these samples were measured with the refractometer. Also, the boiling point of the residue was recorded. Once the distillation was finished, any excess sample and the distillate was added back into the residue flask.

This process was repeated, with the modification of adding 1.0, 2.0, 5.0, 10.0, and 20.0 mL of additional chloroform after each process. For example, before the next full distillation, 1.0 mL of chloroform was added to the residue flask, and samples of residue and distillate were taken again and their refractive indexes were measured. 2.0 mL of additional chloroform was added before the next distillation.

Originally, the experiment was going to be run with an initial residue of chloroform with gradual additions of acetone. However, on the second day of the experiment the following week, the original heating mantle and replacement hot plate were both defective, and the distillation could not begin. As a substitute, data was recovered from a previous run of this experiment.

In the previous run, which would have been identical to this run, 50 mL of chloroform was added to the residue flask, and the same process would have been repeated, except adding 4, 8, 10, 14, and 20 mL of acetone to the residue flask in between distillations. The refractive indexes would have been measured of both the residue and distillate, as well as the boiling point of the residue.

# Results

The first calculation was setting up a calibration curve with the calibration binary solutions. First, the volumes of chloroform and acetone were converted to grams, and then to moles, to calculate the mole fraction of acetone. Then, as the relationship between mole fraction and refractive index is linear, the points were plotted on a graph, and a line of best fit was calculated to create a relationship between the mole fraction of acetone and the refractive index of the binary solutions. This equation, seen on Figure 1, will be used to estimate the mole fraction of the distillates and residues collected in the next part of the experiment.

Equation : Example Conversion of 3mL Acetone/2mL Chloroform Solution to Mole Fraction

Figure : Calibration Curve of Acetone/Chloroform Calibration Solutions

Next, the data recorded combined with the previous experiment’s data was tabulated. Using the measured refractive index and the equation calculated with the calibration plot seen in Figure 1, mole fractions of each distillate and residue were calculated by plugging in y for the refractive index measured and solving for x. After the mole fraction was calculated, each point was plotted on a graph against the measured boiling point of the distillate. Note that residue and distillate are graphed with different legends. As azeotropes are characterized as a solution where the concentration or mole fraction of the solution does not change from the liquid to the vapor phase, an azeotrope would be two points on the graph where the residue and distillate overlap.

Figure : Temperature Composition Diagram of Acetone/Chloroform Binary Solutions

This characteristic overlapping happens between 336 and 333 K, where the mole fraction is 21-28% acetone. Combined with the expectation that the azeotrope will have a maximum or minimum boiling point in this plot, the azeotrope should be closer to 21% acetone. Thus, the azeotrope of this binary solution is determined to be about 21% mole fraction acetone, with a boiling point of 336 K.

# Discussion

In the general case, liquids boil when the vapor pressure of the liquid reaches the pressure of the vapor atmosphere around it. Ideally, a liquid with multiple components will boil when the sum of the partial vapor pressures of the components reaches this atmospheric pressure, as the combined vapor pressure of the liquid would be equal to the atmospheric pressure.

To confirm non-ideal behavior, i.e., the presence of azeotropic behavior, the temperature-composition diagram was calculated if the solution were ideal. Using partial vapor pressure equations from equation 2 along with given constants, a system of equations was set up and a plot was calculated in figure 3.

Equation 2: System of Equations (labeled [1] and [2]) Used for Composition of Binary Mixture at Given Boiling Point

Figure 3: Ideal Temperature Composition Diagram for Acetone/Chloroform Binary Solution

Observing the shape of the curve on Figure 3 compared to Figure 2 clearly shows that there are interactions between chloroform and acetone that make the relationship between mole fraction and boiling point non-linear. This comparison further goes to confirm that an azeotrope is present in this mixture.

Although the second run of the distillation was unable to be completed, the data gathered from a previous experiment were still valid to be used in these calculations, given a few caveats. Azeotropes, also known as constant boiling point mixtures, do not change their compositions as they boil off. The only significant difference in this run of the experiment compared to the previous run would have been the atmospheric pressure of that day. Atmospheric pressure would only marginally affect the measured boiling point of the mixture. Furthermore, it would not change the fact that the mole fraction of the distillate and residue would be identical, as this is by definition of an azeotrope. Therefore, in figure 2, the overlapping of points will still constitute an azeotrope at that mole fraction composition, however, the boiling point may not be exact for the mixture, given the atmospheric pressure for the runs could be different. Thus, given these factors, we can only conclude a possible composition of an azeotrope, and support the idea that chloroform and acetone constitute a negative azeotrope, an azeotrope with a higher boiling point than its pure components.

# Appendix

1. Excel Spreadsheet of Experiment Data 