Liquid - Vapor Equilibrium/Distillation
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Background

The volatility of a compound is its ability to change into a vapor, or to evaporate at a particular temperature and pressure. The normal boiling point of a liquid usually allows comparison of its volatility to other materials, with lower boiling points indicating greater volatility, but this may be affected somewhat by the presence of other materials. Comparison of the concentration ratios in the vapor and liquid states gives a more precise measure of the relative volatility of the components of a mixture. One liter of an aqueous solution (the boiling point of water is 100 °C) containing 1.0 M ammonia (NH₃, boiling point - 33.9°C) and 1.0 M sodium chloride (NaCl, boiling point 1413 °C) has a molar ratio


If the equilibrium vapor above this mixture is collected and analyzed, no sodium chloride is found, and the molar ratio of water to ammonia is less than 4:1. The vapor is depleted in sodium chloride and enriched in ammonia relative to the liquid or solution state, as one might expect from the boiling points. The vapor still has a greater percentage of water than ammonia, but because of the enrichment of ammonia in the vapor relative to the liquid we recognize the greater relative volatility of ammonia in the solution. The presence of an inorganic salt such as sodium chloride usually decreases the volatility of water and increases the volatility of less polar compounds like ammonia, a type of salting-out.

If this solution is heated at atmospheric pressure, it will begin to boil at a temperature slightly less than 100 °C. If a small fraction of the liquid is vaporized, collected, and cooled it will return to the liquid state (condensation) with essentially the same molar ratio as the vapor had. This new liquid will have a much greater concentration of ammonia (about 9 M) than the original solution. The remaining liquid in the boiler (also called the reboiler) which was not evaporated will have a lower concentration of ammonia than the original solution, and a greater concentration of sodium chloride. There is a fairly constant ratio of the concentration in the collected liquid (the condensate or distillate) to the concentration in the liquid from which it was distilled, which we will call a partitioning constant:

\[ K_A = \frac{\text{concentration in condensate}}{\text{concentration in boiler}} \]

This process of vaporizing a liquid and condensing the vapor is called distillation, and has great importance in the separation and purification of materials. If an appreciable amount of the condensate from the example above is heated, it will boil at an even lower temperature than before (because of the greater concentration of the more volatile component) and the vapor will be further enriched in the more volatile component. A distillation column allows this continuous reboiling and condensation, so that the more volatile component becomes increasingly purer or more concentrated as it rises in the column. The degree of separation may be controlled to some extent by the length, temperature, and design of the column. In some cases, the distillation process is limited by a condition in which the concentration ratio in the vapor becomes identical to the concentration ratio in the liquid, resulting in a constant-boiling mixture or azeotrope.

When the distillation involves water and an organic compound, the addition of salts...
can have a dramatic effect. The much greater affinity of the salt for the water causes salting-out of the organic component. This is described with a salting-out coefficient ($k_{salt}$) which depends on both the salt and the organic compound:

$$\ln K = \ln K_0 + k_{salt}C_{salt}.$$  

For a given salt, the salting out coefficient generally increases with increasing non-polar character of the organic molecule. The coefficients for some types of molecules are more dependent on the cation of the salt, while others depend more on the anion.

**VINEGAR**

Vinegar is an aqueous solution of acetic acid, produced by the fermentation of sugar to ethanol, followed by bacterial oxidation of the alcohol to acetic acid:

$$C_6H_{12}O_6 \rightarrow 2 C_2H_5OH + 2 CO_2$$

sugar    ethanol

$$C_2H_5OH + O_2 \rightarrow CH_3CO_2H + H_2O$$

ethanol  acetic acid

The fermentation of fruits such as grapes or apples results in a colored, flavorful product called “wine vinegar” or “apple cider vinegar”. Colored “malt vinegar” is produced from malted grains, and might also be called “beer vinegar”. Commercial processes produce a concentration of acetic acid around 10% (w/w), which may be diluted to a minimum of 4% in the final product. If the second fermentation is conducted with dilute distilled alcohol, the resulting product is a clear, colorless liquid labelled “distilled” vinegar.

In this experiment, the distillation of apple cider vinegar will be followed by analyzing samples from the boiler and the distillate, determining the relative volatility of water, acetic acid, and the colored materials in the vinegar. The effect of added salts will be evaluated. The acidity of the samples will be determined by titration with a standard solution of sodium hydroxide (NaOH).

**Mathematical Analysis:**

In the distillation process, a solute in the liquid phase (mole fraction = $X_A$) is in equilibrium with the vapor phase (partial pressure = $P_A$):

$$X_A \gamma_A = \frac{P_A}{k_A}$$

in which $\gamma_A$ is the activity coefficient in the Henry’s Law System ($k_A$ is the Henry’s Law constant). This can be restated in terms of concentration in the liquid phase,

$$C_A = X_A/V_m$$  ;  \(V_m\) is the molar volume of the liquid phase

and in the vapor phase

$$C_A^v = \frac{P_A}{RT}$$

Combination of Eq (1-3) gives

$$k_A \gamma_A = \frac{P_A}{X_A} = \frac{C_A^v RT}{C_A L V_m L}.$$  

It is easier to consider the vapor phase in terms of what it would be if condensed to distillate:

$$n_A^v = C_A^v n_{tot}^v RT/P_{tot} = C_A^{dist} n_{tot}^v V_{m^{dist}}$$

and
\[ C_A V (RT/P_{tot}) = C_A^{dist} V_m^{dist} \]  \hspace{1cm} (5)

Substituting (5) into (4) gives

\[ (k_A Y_A/P_{tot})(V_m^L/V_m^{dist}) = K_A = C_A^{dist}/C_A^{pot} \]  \hspace{1cm} (6)

in which the concentration in the boiler (\(C_A^{pot}\)) has been substituted for \(C_A^L\). The effective partitioning constant of the solute between between the distillate and the boiler (\(K_A\)) can be expected to remain constant over narrow ranges of the distillation. The value of \(K_A\) can be determined by analysis of the distillate and the boiler for a simple one-stage distillation.

The average value of \(K_A\) can be determined by analysis of the solute in the boiler over a more complex distillation. Starting from the mass balance:

\[ \frac{dn_A^{pot}}{nb} = - C_A^{dist} dV^{dist} = C_A^{pot} K_A dV^{pot} \]  \hspace{1cm} (7)

and

\[ \frac{dn_A^{pot}}{nb} = C_A^{pot} dV^{pot} + V^{pot} dC_A^{pot} \]

gives

\[ \frac{dC_A^{pot}}{C_A^{pot}} = (K_A - 1)(dV^{pot}/V^{pot})\]  \hspace{1cm} (8)

This integrates to

\[ K_A = 1 + [\ln(C_A^{pot}/C_A_{0}^{pot})]/[\ln(V^{pot}/V_0^{pot})] \]  \hspace{1cm} (9)

which is an alternate form of the Butler equation. If \(K_A > 1\) (enriched vapor), the concentration of the solute in the boiler will decrease as material is distilled away.

**Effects of a non-volatile component.**

A non-volatile component, particularly a salt, can affect the value of \(K_A\). The salting-out effect is usually described as

\[ \ln K_A = \ln K_{A,0} + k_{salt} C_{salt} \]  \hspace{1cm} (10)

in which \(K_{A,0}\) is the value observed in the absence of salt, and \(k_{salt}\) is a constant which is characteristic of the salt and the material which is salted-out. Since the non-volatile salt remains in the boiler, it’s concentration increases through the distillation, and the value of \(K_A\) also changes:

\[ K_A = K_{A,0} \exp[k_{salt} C_{salt,0}(V_{0}^{pot}/V^{pot})] \]  \hspace{1cm} (11)

The value of the salting-out coefficient may be determined by evaluating values of \(K_A\) determined at average values of \(C_{salt}\) over a distillation, and plotting \(\ln K_A\) vs \(C_{salt}\).
**Distillation Procedure:** You will study the distillation with and without added salt. Record the molarity of the standard NaOH solution on the data sheet. Samples should be titrated while additional samples are being collected.

1. Measure 50 ml of the stock solution of apple cider vinegar into the round-bottom flask, add a couple of boiling stones, and assemble the apparatus as shown. Slowly bring the solution to a gentle boil, then increase the heat to fairly vigorous boiling. Record the initial volume on the Data Sheet in blank A1.

2. Collect 9-10 ml of the distillate in the graduated cylinder, then switch to a second clean, dry 10-ml graduate and continue the distillation. Record the volume of the sample in blank A2 of the data sheet. Transfer the collected sample to a sample vial labelled Cut #1. Rinse the graduated cylinder and dry it inside and out with a paper towel.

3. When a second aliquot of 9-10 ml of the distillate has been collected, switch to the cleaned and dried graduate and continue the distillation. Record the volume of the sample in blank A3 of the data sheet. Transfer the collected sample to a sample vial labelled Cut #2. Rinse the graduated cylinder and dry it inside and out with a paper towel.

4. Repeat step 3, collecting a third aliquot to be labelled Cut #3, then remove the heat source to stop the distillation. Record the volume of the sample in blank A4 of the data sheet.

5. Allow the boiler to cool somewhat. Transfer the liquid remaining to a 50- or 100-ml graduated cylinder and record the volume in blank A5 of the data sheet. Transfer the sample to a vial labelled Boiler.

6. Rinse and dry all parts of the apparatus.

7. If a salt/vinegar solution is not already prepared, weigh the suggested amount of the salt into a 100-ml volumetric flask and fill to the mark with vinegar. Record the molarity of the salt and the molarity of the NaOH solution on a new data sheet.

8. Repeat steps 1 - 6, collecting aliquots of the distillate from the salted sample. Label these samples as Cut #1S, Cut #2S, etc., to distinguish them from the pure vinegar distillates. Throughout this distillation, watch for the precipitation of salt. There is no point in continuing the distillation if salt begins to precipitate. Salt often appears in the boiler as the solution is cooled after the last cut. This makes the collection of the liquid more difficult, but does not otherwise affect the results.
Titrations:

1. Pipet 5 ml of the stock vinegar or vinegar-salt solution into a 125-ml erlenmeyer flask, add 3 drops of phenolphthalein solution, and about 50 ml of distilled water, and titrate with a standardized 0.25 M solution of sodium hydroxide to a persistent faint pink color. The end point may be difficult to observe because of the color of the sample. Record the volume of the sample (5.00 ml) in blank B1 of the data sheet. Record the initial and final buret readings in blanks Ri and Rf of this column, and perform the calculations of blanks C1, D1, and E1.

3. Titrate a pipetted 5 ml sample (B2) of Cut #1, record the data in blank Ri and Rf, and perform the calculations in blanks C2, D2, and E2 under Cut#1. The value to be entered in blank F2 of this column is the value in blank E2 subtracted from the value in blank E1 of the first column. The value to be entered in blank G2 is the volume collected in this cut (blank A2) subtracted from the value in blank A1 and G1. Perform the calculation for blank H2. Discard the remainder of the sample collected, rinse the graduated cylinder, and dry it with a paper towel.

4. Titrate a pipetted 5 ml sample from Cut#2 and record the data in the third column of the data sheet. The value to be entered in blank F3 of this column is the value in blank E3 subtracted from the value in blank F2. The value to be entered in blank G3 is the volume collected in this cut (blank A2) subtracted from the value in blank G2.

5. Titrate 5 ml of Cut #3, and record the data in the fourth column of the data sheet. The operations in this column are the same as in the third column.

6. Titrate a 5 ml sample of the Boiler sample and enter the results in the last column (Boiler) of the data sheet. The end-point of this titration may be difficult to observe because of the color of the sample. A material balance on the millimoles of acid remaining in the boiler (blank E5) against the calculated amount (blank F4) provides a check on the efficiency of the recovery process in this distillation. Obviously, some of the material is retained in the apparatus.

Stepwise Calculations
1. The concentrations of acid (and salt) in the boiler and in the distillate are obviously changing during the distillation process. The concentration in the distillate is an average of the instantaneous concentrations over the collection period. This is best compared to the average of the concentrations in the boiler from the start to the finish of the collection period (blank I2), which is obtained for Cut#1 by averaging the value in blank H2 with the original composition in the boiler (blank D1). Similarly, the value for blank I3 is obtained by averaging the values in blanks H2 and H3, and a similar calculation is performed for I4. These averaged values of concentrations in the boiler and in the distillate are used to calculate the partitioning constants (K) in blanks J2, J3, and J4. The concentration of salt is followed similarly in blanks L2-L4, and averaged in blanks M2-M4.

2. Spreadsheets (DS_PC7.WS2 - QuattroPro for Windows, DS_PC7 - Excel for Macintosh or Windows) are provided to check and print out your calculations. If your experiment involved a salt, make sure that the name is entered on the spreadsheet. Load the necessary information into the spreadsheet, resolve any differences between the spreadsheet and your data sheet, print copies for the group, and save the file to the
Users/GUEST folder on the ChemNov/UMR-chem-fs1 server. Name your file in the format: **PC7 + Section Letter (A,B,C)+group number (1,2,3,4) + group letter (A or B)=PC7C2A** (Experiment 7 by group 2A of Chem 242C).

References: