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# Vapor-Liquid Equilibrium

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## Overview

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Vapor-liquid equilibrium is paramount in engineering applications such as distillation, environmental modeling, and general process design. Understanding the interactions of components in a mixture is very important in designing, operating and analyzing such separators. The activity coefficient is an excellent tool for relating molecular interactions to mixture composition. Finding the molecular interaction parameters allows future prediction of the activity coefficients for a mixture using a model.

Vapor-liquid equilibrium is a critical factor in common processes in the chemical industry, such as distillation. Distillation is the process of separating liquids by their boiling point. A liquid mixture is fed into a distillation unit or column, then boiled. Vapor-liquid equilibrium data is useful for determining how liquid mixtures will separate. Because the liquids have different boiling points, one liquid will boil into a vapor and rise in the column, while the other will stay as a liquid and drain through the unit. The process is very important in a variety of industries.

In this experiment, the activity coefficients of mixtures of various compositions of methanol, isopropanol, and deionized water will be obtained using a vapor-liquid equilibrium apparatus and gas chromatograph. Additionally, the binary interaction parameters of the system will be determined using Wilson's equation and the activity coefficients.

## Principles

Vapor-liquid equilibrium is a state in which a pure component or mixture exists in liquid and vapor phases, with mechanical and thermal equilibrium and no net mass transfer between the two phases. Vapor and liquid are separated by gravity and heat (Figure 1). The liquid mixture is inserted into the system, which is put into a vacuum state with a vacuum pump. The vapor is condensed and returned to mix with the liquid, which is then passed back to the boiling chamber. Differences in the boiling point results in some separation of the mixture. The boiling point of water is higher than that of the added components, so the volatile components begin to evaporate.
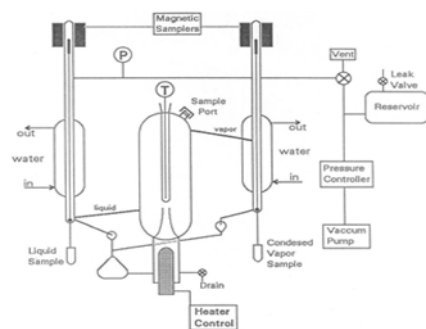
Vapor-Liquid Equilibrium Apparatus



**Figure 1: A depiction of the apparatus**

An activity coefficient is defined as the ratio of a component's fugacity in an actual mixture to the fugacity of an ideal solution of the same composition. Fugacity is a property used to show differences between chemical potentials at standard states. Vapor phase fugacities can be expressed in terms of a fugacity coefficient [$\varphi$: $f_i^V = \varphi_i y_i f_i^{0V}$], with $y_i$ = mol fraction of i in the vapor phase, and $f_i^{0V}$ = the vapor standard state fugacity (the fugacity of pure component vapor at T and P). For low pressures, as in this experiment, $\varphi_i = 1$ and $f_i^{0V} = P$. Liquid phase fugacities can be expressed in terms of an activity coefficient $\gamma_i$: $f_i^L = \gamma_i x_i f_i^{0L}$, with $x_i$ = mol fraction of i in the liquid phase, and $f_i^{0L}$ = the liquid standard state fugacity.

At the saturation pressure ($P_i^s$) of this T, the pure component liquid fugacity would be $P_i^s$, because the pure vapor and liquid are in equilibrium. Since liquid fugacities are only weak functions of pressure, we can approximate the pure component liquid fugacity at T and P ($f_i^{0L}$) as $P_i^s$, as long as the difference between $P_i^s$ and P is not large. This approximation is usually called "neglecting the Poynting correction". If experimenters use a VLE apparatus to measure the compositions of the vapor and liquid which are in equilibrium, experimenters can directly calculate the activity coefficients provided to also measure P and T. T must be measured to determine $P_i^S$ for all i.

The heart of the VLE device, used in this experiment to determine compositions of mixtures, is a Cottrell pump which "spits" boiling liquid into a well-insulated, equilibrium chamber. Two magnetically operated sampling valves allow for withdrawal of liquid and condensed vapor samples. A large reservoir helps to dampen pressure pulses in the system as the on-off control valve switches, and from fluctuations caused by the Cottrell pump. A slow leak can be used to create a balance between the rate of withdrawal of air and the rate of input of air to maintain a constant pressure, if necessary.

A comparable way to solve for vapor-liquid equilibrium is to use a variety of models. Raoult's law, Dalton's law, and Henry's law are all theoretical models that can find the vapor-liquid equilibrium concentration data. All three models are related to the proportionality of partial pressures, total pressure, and mole fractions of substances. Wilson's equation has been proven to be accurate for miscible liquids, while not being overly complex. Additionally, Wilson's model incorporates activity coefficients to account for deviation from ideal values.

## Procedure

## 1. Priming the system

1. Vent the VLE system using the vent/control 3-way valve mounted on the frame of the apparatus, and (if necessary) by draining liquid out of the system into a waste flask.
2. Remove the sample tubes and replace with clean tubes (if necessary). The liquid will not completely drain out of the system.
3. For the first run of experiments, refill through the input valve with a mixture of roughly (vol%) 50 % methanol, 30 % isopropanol and 20 % water. For the second week, refill with roughly 25% methanol, 45% isopropanol and 30% water. For the third week, refill with whatever liquid you need to repeat. The total liquid capacity is approximately 130 cm$^3$.
4. Fill with liquid to just below the spot where the Cottrell pump intersects with the vacuum jacket. Too little liquid will cause the system to require very high boiling rates to get enough liquid to "spit" (when liquid pops while boiling intensely).
5. Use a beaker and pour the liquid into the addition port at the top of the equilibrium chamber. Close the port.
6. Check the barometric pressure with the mercury manometer on the wall. Adjust the "zero" on the digital pressure gauge to match (if necessary).
7. Switch the three-way vent valve to "control" and start up the vacuum pump and pressure controller.
8. Open the throttle valve on the pressure controller several turns and observe the pressure rapidly drop. Watch the pressure on the digital pressure gauge.
9. Set the control pressure set-point on the pressure controller to obtain ~ 700 mm. Listen for clicking of the control valve. Once the control point is reached, the noise from the vacuum pump will be audibly different.
10. At this point, with the throttle valve opened several turns, every time the control valve opens, too much air is dumped to the vacuum pump and the pressure dips below 700 mm before slowly recovering. Close the throttle valve completely, then open it about ½ turn.
11. Wait for the control valve to begin clicking again, then close the throttle valve in small increments until the pressure fluctuates only ~0.5 mmHg or less when the valve is open. Make minor adjustments to the control point or the leak valve as necessary to maintain very near 700 mmHg.
12. Once the mixture is within ±10 mmHg of 700 mmHg, turn on the heater power, heating mantle power, condenser water and magnetic stirrer. Try 25-30 % heater power and 1.5-2 turns mantle power to start. The apparatus will require 20 min or less to approach equilibrium. Keep adjusting the pressure during this time.

## 2. Running the experiment

1. Upon boiling, the Cottrell pump will begin to spit liquid and liquid can be seen dripping back into the boiling chamber. Condensed vapor will require longer to appear. When equilibrium is reached, experimenters should see steady drips of condensed vapor (2-3 drops/s) and returned liquid (2-3 drops/s). The temperature should be stable to ±0.03ºC and the pressure should be stable at 700.0 ± 0.5 mmHg. When these conditions have been established for at least 2 min (or so), equilibrium is attained.
2. Open the magnetic valves (marked "1" and "2" on the controller) 4 or 5 times each for long enough to collect about ½ cm$^3$ of liquid in each sample tube, and close the tubes. If a valve does not respond to its button, try flipping the power switch for the controller off then on. This first sample will be used to wash the tubes and delivery system and will be discarded. Washing replaces any remaining chemical on the sides of the tubes with the same chemical that is being sampled, so it will not affect the composition of the test.
3. Momentarily turn off the power to the heater, wait 30 seconds for the boiling to subside, then vent the system with the vent/control 3-way valve. Remove the sample tubes, swirl a few times, then dump them into the waste pot.
4. Refit the sample tubes on the system, turn the vent valve back to "control", turn the power back on to the heater, and wait for equilibrium to be reestablished. This will only take a few min if the apparatus does not cool. A slight difference in temperature may be observed when equilibrium is re-established. This can be due to a slight disturbance of the overall composition due to sampling.
5. Once equilibrium is re-established, take two new samples. Have two labeled vials with new septa ready.
6. After taking ~0.5 cm$^3$ samples in each tube again, turn off the heater, vent the system, remove the sample tubes and pour them into the vials. Cap the vials and replace the sample tubes with clean tubes if necessary.
7. While analyzing the samples, prepare a new sample. Drain ~15 cm$^3$ of liquid into a beaker or flask. Add ~20 cm$^3$ of pure methanol or 50/50 methanol/isopropanol through the sample port. This will give a new overall composition.
8. Be sure the sample tubes are completely empty, then close the system off, switch the vent valve to "control", and turn the heater back on. If working quickly, equilibrium will be re-established rapidly. Note that there should be a temperature difference from the previous sample.
9. Repeat the equilibration and sampling procedure as before, remembering to take one sample to wash, and then take the final sample. Continue the experiments by adding component(s). Twelve data points are sufficient to determine the activity coefficients and (roughly) the binary interaction coefficients.

## 3. Shutting down the system

1. Turn the heaters off. When the apparatus begins to cool, shut off the stirrer and condenser water.
2. Return the system to atmospheric pressure; set the controller >1020 mbar, close the throttle valve, set the three-way valve to vent and open the valve on the tank.

3. Once atmospheric pressure has been reached, shut off the pump. Drain the liquid from the reservoir until it reaches the level of the valve, but leave the rest of the liquid in the reservoir. Close the 3-way valve.

# 4. Analysis

1. Using nonlinear regression and a standard sum of squared residuals objective function, use the activity coefficients computed from the raw data to regress the 6 constants for the ternary Wilson equation (below), for this system. Assess the quality of the fit by graphical methods and computing the average percent relative deviations (APRD), which are average fit errors x 100.

$$\ln \gamma_k = 1 - \ln\left(\sum_{j=1}^{m} x_j \Lambda_{kj}\right) - \sum_{i=1}^{m} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{m} x_j \Lambda_{ij}}$$

2. Converge on the true optimal values from several different directions in response parameter space by using a factorial method for the initial guesses. Compute the precision of the GC measurements by sufficiently replicating one GC sample to determine relative precisions according to the t-statistic, and use the precisions to determine whether to accept / reject a particular GC measurement by appropriate hypothesis test.
3. Compare the relative precisions of the GC measurement to the APRDs, and discuss. Also report the absolute precisions of the pressure and temperature gauges - determine these once per day.

## Results

The activity coefficients of the data do not show significant deviations from a mean value for each component (Table 1). This is as expected because for intermediate component compositions there are not large variations. However, components near 1 have γ's near 1. Low composition components have high γ's. Components highest in concentration in a mixture which will have a reduced deviation, therefore it will be closer to ideal (γ = 1). Components with lower concentrations in a mixture will have higher deviations, so their γ's will be greater than 1.

**Experimental Equilibrium Data**

| Temp | Liquid Mole Fraction (AVG), $x_i$ | | | Vapor Mole Fraction (AVG), $y_i$ | | | Saturation Pressure, $P^{sat}$ (mm HG) | | | Experimental Activity Coeff. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (°C) | $H_2O$ | MeOH | IPA | $H_2O$ | MeOH | IPA | $H_2O$ | MeOH | IPA | $H_2O$ | MeOH | IPA |
| 72.84 | 0.42 | 0.46 | 0.13 | 0.22 | 0.66 | 0.13 | 264.06 | 1046.03 | 515.76 | 1.37 | 0.96 | 1.41 |
| 69.90 | 0.29 | 0.62 | 0.09 | 0.14 | 0.79 | 0.07 | 232.80 | 936.33 | 454.52 | 1.44 | 0.95 | 1.22 |
| 75.32 | 0.19 | 0.66 | 0.15 | 0.16 | 0.70 | 0.14 | 293.12 | 1146.64 | 572.67 | 2.01 | 0.65 | 1.15 |
| 68.84 | 0.20 | 0.68 | 0.12 | 0.10 | 0.82 | 0.08 | 222.32 | 899.20 | 434.00 | 1.61 | 0.93 | 1.11 |
| 67.05 | 0.14 | 0.78 | 0.08 | 0.07 | 0.88 | 0.05 | 205.53 | 839.28 | 401.11 | 1.62 | 0.94 | 1.13 |
| 76.22 | 0.52 | 0.26 | 0.22 | 0.30 | 0.41 | 0.28 | 304.31 | 1185.08 | 594.58 | 1.34 | 0.93 | 1.55 |
| 75.38 | 0.47 | 0.30 | 0.23 | 0.28 | 0.46 | 0.27 | 293.86 | 1149.17 | 574.11 | 1.41 | 0.92 | 1.43 |
| 74.55 | 0.41 | 0.34 | 0.24 | 0.25 | 0.49 | 0.26 | 283.83 | 1114.58 | 554.46 | 1.52 | 0.90 | 1.32 |
| 73.94 | 0.36 | 0.38 | 0.26 | 0.22 | 0.54 | 0.24 | 276.64 | 1089.71 | 540.39 | 1.54 | 0.90 | 1.23 |
| 73.44 | 0.32 | 0.41 | 0.27 | 0.20 | 0.56 | 0.24 | 270.86 | 1069.67 | 529.07 | 1.63 | 0.89 | 1.17 |

**Table 1: Results of each sampling of the experimental data.**

The data was fit to Wilson model parameters and the coefficients were calculated (Table 2). A simple reduction in the sum of squared residuals between experimental and Wilson equation (1) activity coefficients was used. This was achieved using Excel's solver function. The parity plot shown relates the Wilson's Equation model activity coefficients to the experimentally found activity coefficients. The experimental activity coefficients were calculated and graphically compared to the calculated model coefficients.

**Model Fitting**

| Temp | Liquid Mole Fraction (AVG), $x_i$ | | | Vapor Mole Fraction (AVG), $y_i$ | | | Experimental Activity Coeff. | | | Model Activity Coefficient, $\gamma_i$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (°C) | $H_2O$ | MeOH | IPA | $H_2O$ | MeOH | IPA | $H_2O$ | MeOH | IPA | $H_2O$ | MeOH | IPA |
| 72.84 | 0.42 | 0.46 | 0.13 | 0.22 | 0.66 | 0.13 | 1.37 | 0.96 | 1.41 | 1.39 | 1.01 | 1.47 |
| 69.90 | 0.29 | 0.62 | 0.09 | 0.14 | 0.79 | 0.07 | 1.44 | 0.95 | 1.22 | 1.48 | 1.00 | 1.24 |
| 75.32 | 0.19 | 0.66 | 0.15 | 0.16 | 0.70 | 0.14 | 2.01 | 0.65 | 1.15 | 1.70 | 0.98 | 1.06 |
| 68.84 | 0.20 | 0.68 | 0.12 | 0.10 | 0.82 | 0.08 | 1.61 | 0.93 | 1.11 | 1.64 | 0.99 | 1.08 |
| 67.05 | 0.14 | 0.78 | 0.08 | 0.07 | 0.88 | 0.05 | 1.62 | 0.94 | 1.13 | 1.66 | 0.99 | 1.00 |
| 76.22 | 0.52 | 0.26 | 0.22 | 0.30 | 0.41 | 0.28 | 1.34 | 0.93 | 1.55 | 1.38 | 0.98 | 1.57 |
| 75.38 | 0.47 | 0.30 | 0.23 | 0.28 | 0.46 | 0.27 | 1.41 | 0.92 | 1.43 | 1.45 | 0.97 | 1.45 |
| 74.55 | 0.41 | 0.34 | 0.24 | 0.25 | 0.49 | 0.26 | 1.52 | 0.90 | 1.32 | 1.53 | 0.96 | 1.33 |
| 73.94 | 0.36 | 0.38 | 0.26 | 0.22 | 0.54 | 0.24 | 1.54 | 0.90 | 1.23 | 1.61 | 0.95 | 1.25 |
| 73.44 | 0.32 | 0.41 | 0.27 | 0.20 | 0.56 | 0.24 | 1.63 | 0.89 | 1.17 | 1.68 | 0.94 | 1.19 |

**Table 2: Results of fitting the data to the Wilson model parameters.**

$$\ln \gamma_k = 1 - \ln\left(\sum_{j=1}^{m} x_j \Lambda_{kj}\right) - \sum_{i=1}^{m} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{m} x_j \Lambda_{ij}} \quad (1)$$

The parameter values found were the best fit (Table 3). Ideally the correlation is along the y=x line; however, a significant correlation resembling the ideal scenario was found (**Figure 2**). The activity coefficients of the data did not show significant deviations from a mean value for each component, as expected. A reduction in the sum of squared residuals between experimental and Wilson equation activity coefficients was used with Excel's solver function. The parity plot relates the Wilson's Equation model activity coefficients to the experimentally found activity coefficients.

|  | Sum of Residuals Squared |
| --- | --- |
| SS = | 0.28 |

| Converged Model Parameters | |
| --- | --- |
| Water (a), MeOH (b), IPA (c) | |
| $\Lambda$ ab= | 0.839 |
| $\Lambda$ ba= | 0.639 |
| $\Lambda$ ac= | 0.762 |
| $\Lambda$ ca= | 0.071 |
| $\Lambda$ bc= | 2.347 |
| $\Lambda$ cb= | 0.309 |

**Table 3: Model parameters with water (a), MeOH (b), and IPA (c). The experimental values are compared to expected values**.
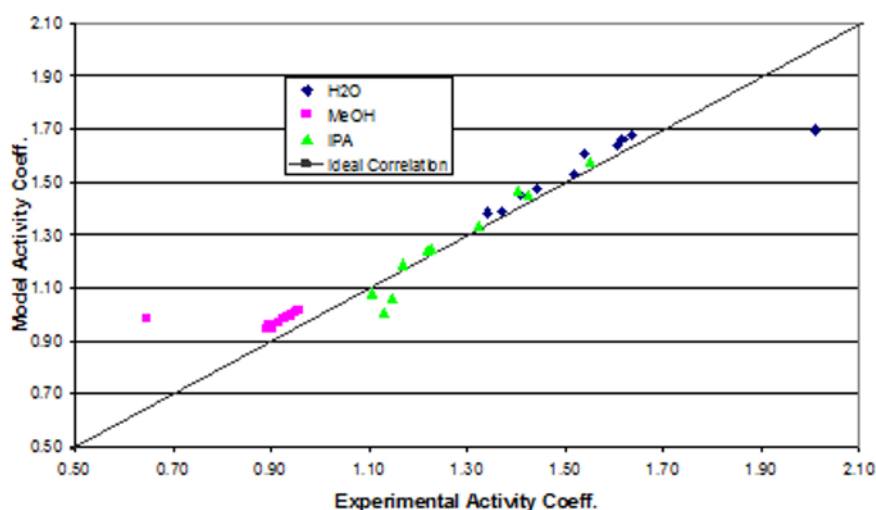


**Figure 2: Depiction of the correlation between the experimental activity coefficients and the model activity coefficients.**

## Applications and Summary

This experiment demonstrated the equilibration of methanol - isopropanol - water vapor-liquid mixtures at a constant P = 700 mm Hg and how to measure temperature and composition and calculate activity coefficients. The activity coefficients of the data did not significantly deviate from a mean value for each component, as expected. A reduction in the sum of squared residuals between experimental and Wilson equation activity coefficients was used with Excel's solver function. The parity plot relates the Wilson's Equation model activity coefficients to the experimentally found activity coefficients.

In the petroleum industry, distillation is the primary process for separation of petroleum products. Many oil refineries use distillation for crude oil[1]. Light hydrocarbons are separated from heavier particles, separating based on boiling points[1]. Heavy materials like gas oils collect in the lower plates, while light materials like propane and butane rise up[1]. Hydrocarbons, such as gasoline, jet, and diesel fuels, are separated[1]. This process is often repeated many times to fully separate and refine the products[1]. Refineries run these processes at steady state, constantly creating new products at maximum capacity, so efficiency is key[1]. Chemical engineers working on these processes focus on optimizing the efficiency of the production[1].

Tray distillation columns are also used to separate a variety of chemical products. Ethanol is one such product. Through closely related processes, a variety of products such as fuel-grade ethanol, beer, and liquor can all be distilled[2]. Specific amounts of alcohol can be separated from water in order to create a specific proof[2]. This process is limited to reducing the percentage of water in the product, but cannot completely eliminate it[2]. In order to remove water completely, azeotropic distillation is required, which uses extractor chemicals to separate water from ethanol[2].

## References

1.  About the Refinery." *Processing & Refining Crude Oil*. Chevron.com, n.d. Web. 17 Nov. 2016.
2.  Madson, PW. *Ethanol Distillation: The Fundamentals*. Cincinnati: Katzen International, n.d. Print. Accessed from Web. 01 Oct. 2016.