THERMODYNAMICS AND TRANSPORT LABORATORY

MIXTURE VAPOR/LIQUID EQUILIBRIUM PRELAB

Ch En 385 – Knotts

Lab Learning Objectives

1. Understand how experimental VLE data are measured using an ebulliometer.
2. Be able to obtain activity coefficients from experimental VLE data.
3. Explain the phase behavior of a binary mixture.

Theoretical Background (Linking to and Expanding upon Previous Knowledge)

A large portion of any chemical process involves the separation of mixtures to make pure chemical species. In most chemical processes, the compound of interest is found in a mixture of chemicals that is supplied by nature (e.g. flecks of gold amid sand; dirt; iron; etc., C5-C10 organic molecules (gasoline) within crude oil) or was the result of a chemical reaction involving many other species (e.g. ethanol from a mixture of water, yeast, cell nutrients, etc.). The desired compounds must therefore be separated from the others in the mixture to be of value.

Many separation processes use differences in phase behavior to purify individual species in the mixture. For example, in many parts of the world salt is obtained from sea water. The sea water (a mixture) is pumped into a settling pool, and the water is allowed to evaporate. This works because the phase behavior of water is very different from that of salt. Water has a much higher vapor pressure than salt (it evaporates *much* more quickly than salt) and it has a lower melting point (water melts at 0 °C while salt melts at 800 °C).

Differences in vapor pressure are widely used in chemical process industries and is the key physics behind distillation. When a mixture of liquids is heated sufficiently to boil, the more volatile components will vaporize at a higher rate than those that are less volatile—enriching the former in the vapor phase and the latter in the liquid phase. However, vapor pressures alone do not tell the entire story as to what is more and less "volatile." In Ch En 373 you learned that low pressure (less than 15 bar) vapor/liquid equilibrium is mathematically described by

$$x_i \gamma_i P_i^{sat}(T) = y_i P$$

where x_i is the mole fraction of component i in the liquid phase, y_i is the mole fraction of component i in the vapor phase, P_i^{sat} is the vapor pressure of component i at system temperature T, P is the pressure of the system, and γ_i is the liquid phase activity coefficient of component i.

Experiments must be done to obtain activity coefficients. The most common experiments are those for binary mixtures. The two compounds are placed into a vessel and brought to a temperature and pressure such that both vapor and liquid phases are present. The compositions of the liquid and vapor phases are then measured. The experiment thus yields values for x_i, y_i, T, and P. The pure component vapor pressure is obtained from an Antione or Riedel correlation,[1] and the activity coefficient is then obtained from

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}}$$

You should recall from Ch En 373 that activity coefficients are strongly dependent on composition (x_i) and weakly dependent on pressure and temperature. Thus, many experiments at different compositions are needed to fully

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[1] You learned how to measure pure component vapor pressures in the "Pure Component Phase Behavior" lab.

characterize γ_i from $x_i = [0,1]$. Such data are then *reduced* by fitting the values for γ_i to an *activity coefficient model* such as van Laar, Wilson, or NRTL.

Prepare for a Safe Experiment (Do This Before the Lab)

Task 1: Read and Commit to Follow the General Lab Safety Rules

1. No food or drink is allowed in the laboratory.
2. All personnel in the laboratory area are required to wear safety glasses, long pants, and covered shoes (no sandals or flip-flops).
3. Experimental work should be completed during the regular class periods. If additional time is needed in the laboratory, you must clear it with your instructor and make an appointment to use the laboratory with a TA. At least two students must be present during those additional hours. (No one is permitted to work in the lab alone).
4. At least two students from each team must be physically in the lab when running experiments. These students should be monitoring the experiment so that emergency procedures can be enacted if problems occur.
5. Students who operate *any* equipment in *any* unsafe manner or in a manner that damages the equipment or results in a user-preventable accident will incur a *significant* grade penalty. This includes not knowing how to run the equipment or shut it down as per instructions provided. *All team members are required to know how to safely run the equipment as instructed.*

Task 2: Become Informed about the Chemicals

- Ethanol: According to its SDS, ethanol is highly flammable. It is also acutely toxic if swallowed, can cause damage to internal organs through repeat exposure, and can harm unborn children. In case of skin contact, rinse the affected area with soap and water.
- Cyclohexane: According to its SDS, cyclohexane is extremely flammable. Avoid breathing in the vapors as they will irritate your respiratory tract. If you begin to feel drowsy or dizzy, move to fresh air. May cause skin irritation. In case of skin contact, rinse the affected area with plenty of water. If it gets in your eyes, flush with water for 15 minutes and get medical help.

Do the following.

A. Download the SDS for ethanol and cyclohexane.
B. Review the SDS of each compound and identify potential hazards. Pay attention to the following:
    - Hazard Statement found in Section 2.
    - Precautionary Statements found in Section 2.
    - NFPA “Safety Square” found in Section 2.
    - First Aid Measures found in Section 4.
C. Commit to handle the compound safely.

Task 3: Review the Following Lab-specific Safety Statements and Procedures

- As with most organic solvents, you should wear gloves while operating the experimental apparatus or handling the chemicals.
- Do not open the Liquid Fill Cap (see the Apparatus section below) while the system is hot. This will release ethanol and cyclohexane vapors into the room.

Task 4: Learn about the Lab Equipment

Apparatus

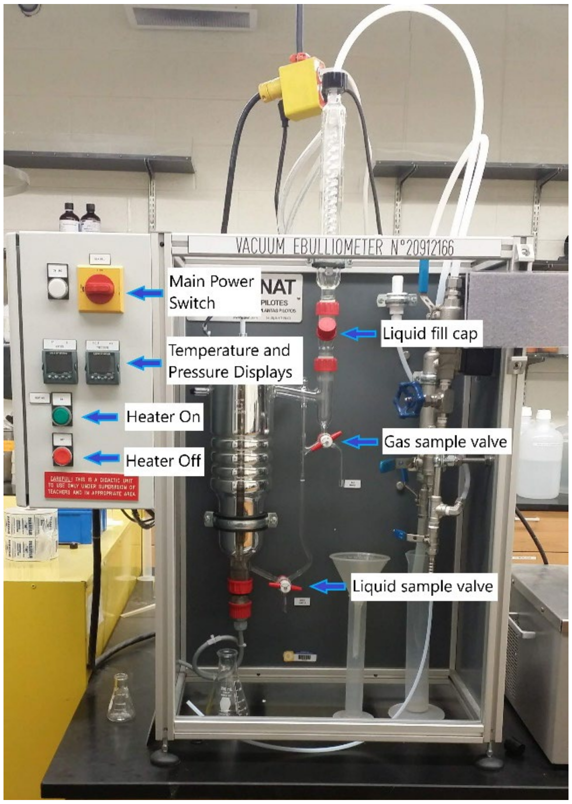


Figure 1 Ebulliometer Apparatus

An eFigure 1 is a picture of the apparatus. Notice the following.

- The main power switch
- Heater On button
- Heater Off button
- Liquid fill cap
- Default valve position
- Temperature and Pressure displays

Figure 2 is a picture of the refractometer. This will be used to measure sample composition by Refractive Index.

Taking Data

- Collecting Samples
- Gas Sample
  - Place vial under outlet from Gas sample valve
  - Turn gas sample valve so line indicate flow from above the valve to the sample outlet
  - Collect between 0.5 – 1 mL
  - Return the valve to default position
- Liquid Sample
  - Place waste container under liquid sample valve
  - Turn valve so that the lines indicate flow from the bottom of the ebulliometer to the liquid sample outlet
  - Drain 15 – 25 mL into the waste container before collecting a sample
  - Turn the valve so that flow stops, but do NOT return the valve to default position as this will result in contamination of the liquid sample with the returning gas sample
  - Place sample vial under the liquid sample outlet
  - Turn valve so that the lines indicate flow from the bottom of the ebulliometer to the liquid sample outlet
  - Collect between 0.5 – 1 mL
  - Return the valve to default position

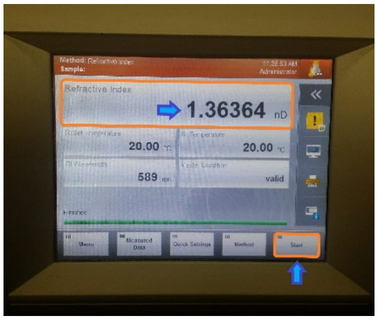
Figure 2 Refractometer

- Reading Refractometer
  - These steps apply to the samples from the gas and liquid composition in the ebulliometer
  - Remove the cover from the sample well
  - Using a disposable pipette, apply several drops of sample liquid to the sample well of the refractometer, filling the well about halfway.
  - Replace the cover on the sample well and press the “Start” button on the interface (If the interface appears blank, press anywhere on the screen and the interface will appear.)
  - After a few moments the device will display the measured refractive Index
  - Record the refractive index in your data table

Analyzing Data

In addition to the data point you take, you will receive a set of data points that was taken by a team of students working in the lab.

Use the calibration curve found on the UO Lab website to determine composition from the Refractive Index, found here: https://uolab.groups.et.byu.net/files/Ebulliometer_calibration_curve.xlsx



Method: Refractive Index
Sample:
Administrator
Refractive Index 1.36364 nD
RI Set Temperature 20.00 °C
RI Temperature 20.00 °C
RI Wavelength 589 nm
Paste Condition valid
Finished

Figure 3Refractometer User Interface

Figure 4Refractometer Sample Well

Figure 5Refrigeration unit for chilled condenser fluid