



Simplified apparatus for vapor-liquid equilibrium
by Trudy Ann Scholten

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Knowledge of the equilibrium behavior of liquid and vapor phases is necessary for proper sizing and design of distillation systems. A novel vapor-liquid equilibrium still was designed to be easy to construct, operate, and clean, while yielding thermodynamically consistent data. The still was constructed and tested using two binary systems. These systems were chosen based on their thermodynamic characteristics, p-Xylene/m-xylene at 635 mmHg, with a temperature range of 129.5°C to 133.0°C, was chosen to represent a thermodynamically ideal system. Benzene/isopropyl alcohol at 640 mmHg, with a temperature range of 67.5°C to 77.9°C, was chosen to represent a nonideal, azeotropic system. Data collected for the p-xylene/m-xylene system was seen to be ideal. Three forms of the Gibbs-Duhem equation were used to evaluate the thermodynamic consistency of the data collected for the benzene/isopropyl alcohol system. The results of these tests indicate that the still design produces consistent data. Wilson parameters obtained from experimental data were seen to be slightly superior to those obtained from literature data.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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TABLE OF NOMENCLATURE

Latin Symbols

a_{12}, a_{21}	Temperature-dependent Wilson parameters
A, B, C	Antoine coefficients
c	Constant of integration
G_{12}, G_{21}	Wilson parameters
h^α	Enthalpy of liquid phase
h^β	Enthalpy of vapor phase
Δh	Change in enthalpy
P	Total pressure
P°	Vapor pressure
p_i	Partial pressure of component i
Q	Function for combining binary system data
R	Universal gas constant
T	Absolute temperature (K)
t	Temperature ($^\circ\text{C}$)
v^α	Specific molar volume of liquid phase
v^β	Specific molar volume of vapor phase
x_i	Liquid fraction of component i
y_i	Vapor fraction of component i

Greek Symbols

γ_i	Activity coefficient of component i
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Subscripts

p	<i>p</i> -xylene
b	benzene

ABSTRACT

Knowledge of the equilibrium behavior of liquid and vapor phases is necessary for proper sizing and design of distillation systems. A novel vapor-liquid equilibrium still was designed to be easy to construct, operate, and clean, while yielding thermodynamically consistent data. The still was constructed and tested using two binary systems. These systems were chosen based on their thermodynamic characteristics. *p*-Xylene/*m*-xylene at 635 mmHg, with a temperature range of 129.5°C to 133.0°C, was chosen to represent a thermodynamically ideal system. Benzene/isopropyl alcohol at 640 mmHg, with a temperature range of 67.5°C to 77.9°C, was chosen to represent a non-ideal, azeotropic system. Data collected for the *p*-xylene/*m*-xylene system was seen to be ideal. Three forms of the Gibbs-Duhem equation were used to evaluate the thermodynamic consistency of the data collected for the benzene/isopropyl alcohol system. The results of these tests indicate that the still design produces consistent data. Wilson parameters obtained from experimental data were seen to be slightly superior to those obtained from literature data.

INTRODUCTION

Knowledge of the equilibrium behavior of liquid and vapor phases is necessary for proper sizing and design of distillation systems [1]. For example, it is absolutely essential to be aware of the presence of any azeotropes or pinch points, as normal rectification cannot efficiently separate the components in these systems [2]. Very few systems exist that may be described accurately with purely theoretical calculations. The remaining systems must be evaluated experimentally. In addition, in extractive and azeotropic distillation, the addition of a solvent or azeotropic agent can dramatically change the equilibrium behavior of the system. In these cases, some systems are susceptible to polymerization. Therefore, it would be especially useful to have a still to obtain vapor-liquid-equilibrium data that is easy to construct, operate, and clean, yet yields consistent data.

Purpose of Research

The purpose of this research was to create a novel VLE still that produces accurate data, is inexpensive to construct, as well as easy to operate and clean. Many existing stills

were evaluated and most favorable aspects combined in the creation of this still. Once this design was achieved, the still was then constructed and tested for thermodynamic consistency, using two systems, *p*-xylene/*m*-xylene and benzene/isopropyl alcohol. These systems were chosen based on their thermodynamic characteristics. The system *p*-xylene/*m*-xylene was chosen to represent a thermodynamically ideal system, while benzene/isopropyl alcohol was chosen to represent a non-ideal, azeotropic system.

Methods of Obtaining Experimental VLE Data

Equilibrium relations may be determined experimentally in several ways. These may be classified as follows [3]:

- 1) Distillation method
- 2) Static method
- 3) Dew and Bubble point method
- 4) Flow method
- 5) Circulation method

The distillation method involves distilling a small amount from a large charge in a boiling flask. By using a large charge, the liquid fraction remains essentially constant, thus approximating an equilibrium condition. Although very simple, this method is seldom used, as it requires a large amount of initial liquid charge and is subject to considerable error [3].

The static method charges a binary mixture to a closed, heated chamber and mixes until equilibrium is established between the liquid and vapor phases. Since small changes in pressure or volume can have significant effects on the system, it is very difficult to

remove samples for analysis without disturbing equilibrium. This method is generally used only at high pressures, since at low to moderate pressures there are easier methods to remove accurate samples.

Using the dew and bubble point method, the dew and bubble point pressures of a mixture of known composition are measured, yielding a pair of points for each composition. Given enough pairs of this type, a vapor (dew point) curve and a liquid (bubble point) curve may be drawn by connecting these points, yielding a P-x-y diagram. An example of this type of graph is shown in Figure 1. This method is generally only applied to light (low molecular weight) hydrocarbons.

The flow method continuously feeds a steady stream of known composition to an equilibrium chamber where it is heated to boiling. After the liquid and vapor streams exiting the equilibrium chamber reach steady state, as evidenced by their temperature and pressure remaining constant, samples are taken and analyzed. This method may yield very precise results, but requires fairly complicated equipment. Further drawbacks include the possibility of long equilibration times and large liquid volume requirements.

Finally, the circulation method is the most widely used method. It is the basis of the experimental still described later in this paper. In the circulation method, vapors coming off a boiling mixture in the liquid chamber are condensed, and this condensate is returned to the liquid chamber, creating a continuous cycle (see Figure 2) [3]. A pseudo-equilibrium steady state is eventually achieved, indicated by the temperature and pressure remaining constant.

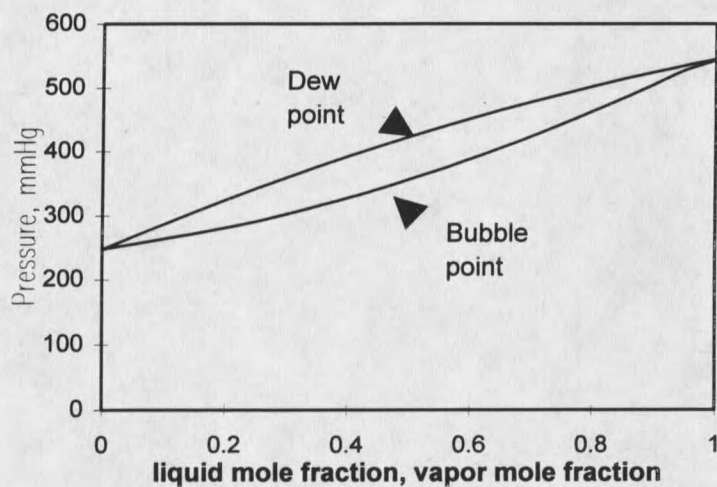


Figure 1: Sample pressure-liquid mole fraction-vapor mole fraction diagram ethanol/propanol, 70°C [16].

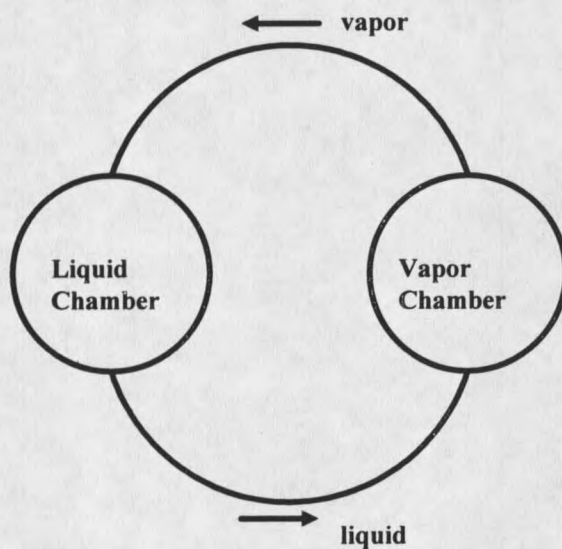


Figure 2: Schematic of circulation method for vapor-liquid equilibrium measurement[3]

Circulation-Type Stills

The first circulation-type vapor-liquid equilibrium (VLE) still to be used successfully was the Othmer still shown in Figure 3 [4]. Operation of the Othmer still begins with a liquid charge heated to boiling in chamber A. Vapors coming off this liquid travel through the vapor tube, past the thermowell, to the condenser. Condensate is collected below the condenser in chamber B, and returned to the boiling liquid via the connecting tube. This design is still widely used today. However, in its unmodified form, the Othmer still has several potential sources of error. The only temperature measurement is of the vapor directly above the liquid. This may be inaccurate, due to condensation on the thermowell. The still contains a fairly large vapor space, and partial condensation may occur on the walls of this vapor space, resulting in more than one theoretical stage. This may lead to incorrect vapor samples, since the vapor composition measured may be a mixture of the vapor coming off the liquid in the flask and the vapor coming off the condensate on the walls. No mechanical mixing of the boiling liquid exists, creating the possibility of concentration gradients in the liquid, possibly producing inaccurate liquid samples. Another concern about the accuracy of the Othmer still is the possibility of mixing between the liquid phase and the returning condensate in the sampling loop if liquid levels are not adjusted correctly. Finally, the amount of condensate required implies a long equilibration time for accurate results.

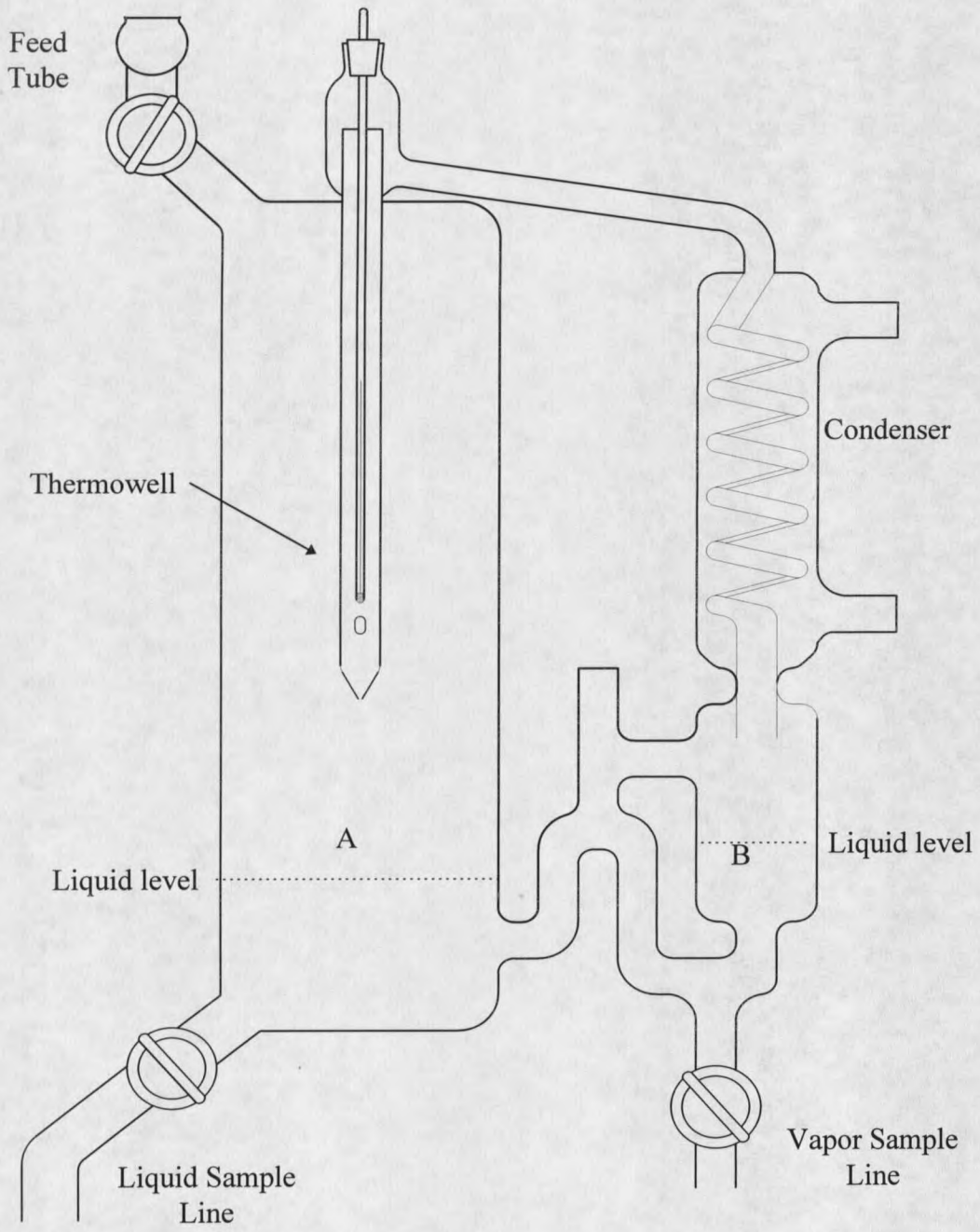


Figure 3: Othmer VLE still [4].

A number of alternative designs are also in use today. Possibly the most common of these is the Stage and Muller still shown in Figure 4 [5], which has been produced commercially. Although this still is generally considered to be quite accurate, it is a fairly complicated design. In this design, liquid is boiled in chamber A. A mixture of vapor and entrained liquid rises through P to the vapor space, V. The vapor space is surrounded by an evacuated jacket, intended to reduce condensation on the walls. The liquid and vapor phases are separated in the vapor space, and returned to A. The two solenoid actuators control the glass ball valves. These valves control the flow path of the returning streams. Liquid samples are collected in chamber E, while vapor condensate samples are collected in chamber F. The number of small tubes in the still result in a difficult cleaning problem. This is considered to be a major drawback of this type of still.

The Kortüm still (Figure 5) is a modification of the Othmer still [3]. The liquid is heated in chamber A by circulating fluid in the jacket of the chamber, as well as by a platinum resistance heater in the liquid. Vapor leaves the top of chamber A and is condensed as it flows towards chamber B. The funnel N is positionable, and can be placed such that liquid flows directly back to chamber A, or into chamber C for sampling. Liquid samples are taken through the capillary tube V, fitted with a rubber bulb. This design has the advantage of being able to take vapor samples from chamber C without interrupting the circulation. Drawbacks of this design include inaccurate temperature measurement, complicated construction, and the possibility of flashing part of the liquid sample during removal from the boiling flask.

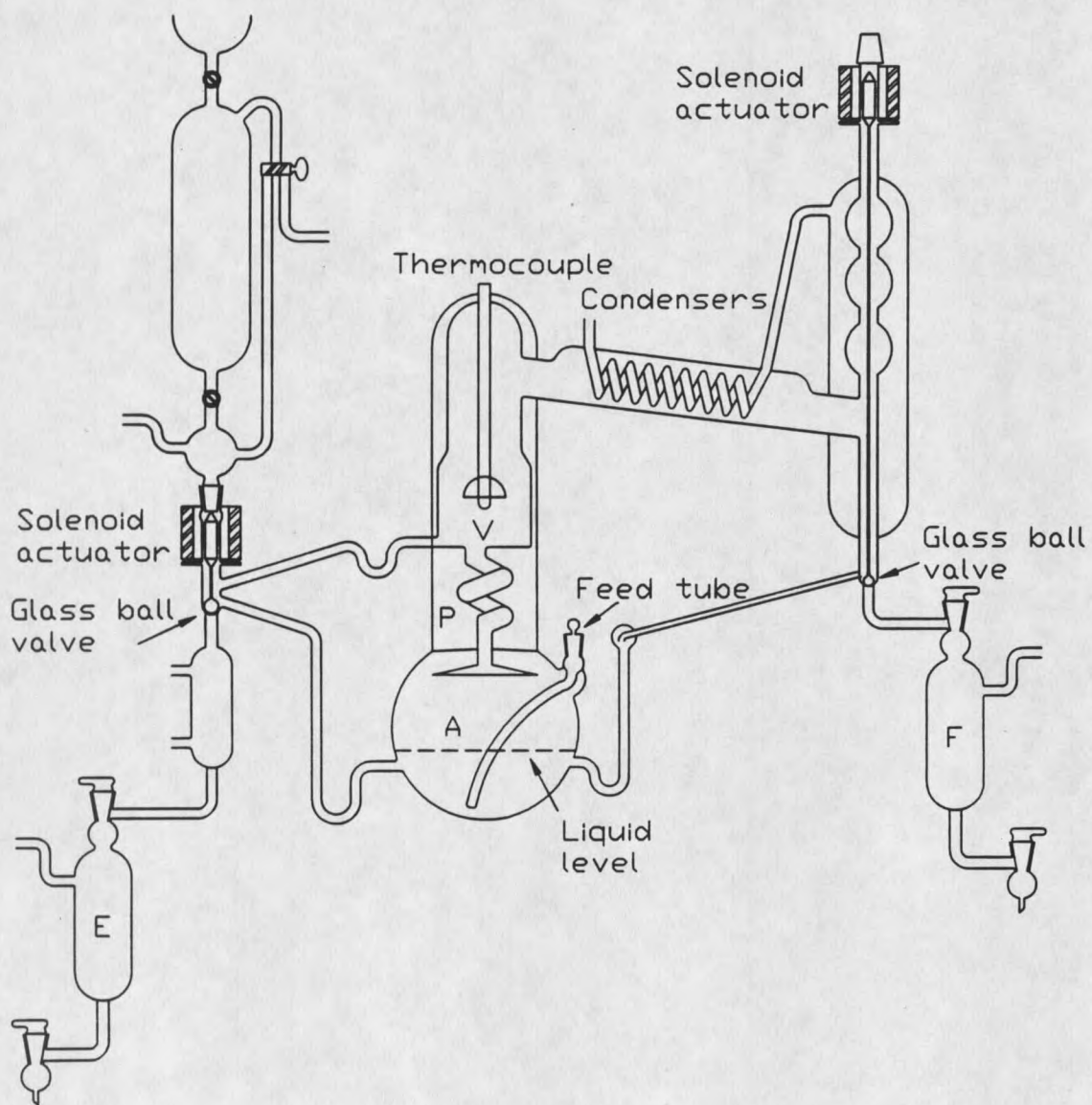


Figure 4: Stage-Müller VLE still [5].

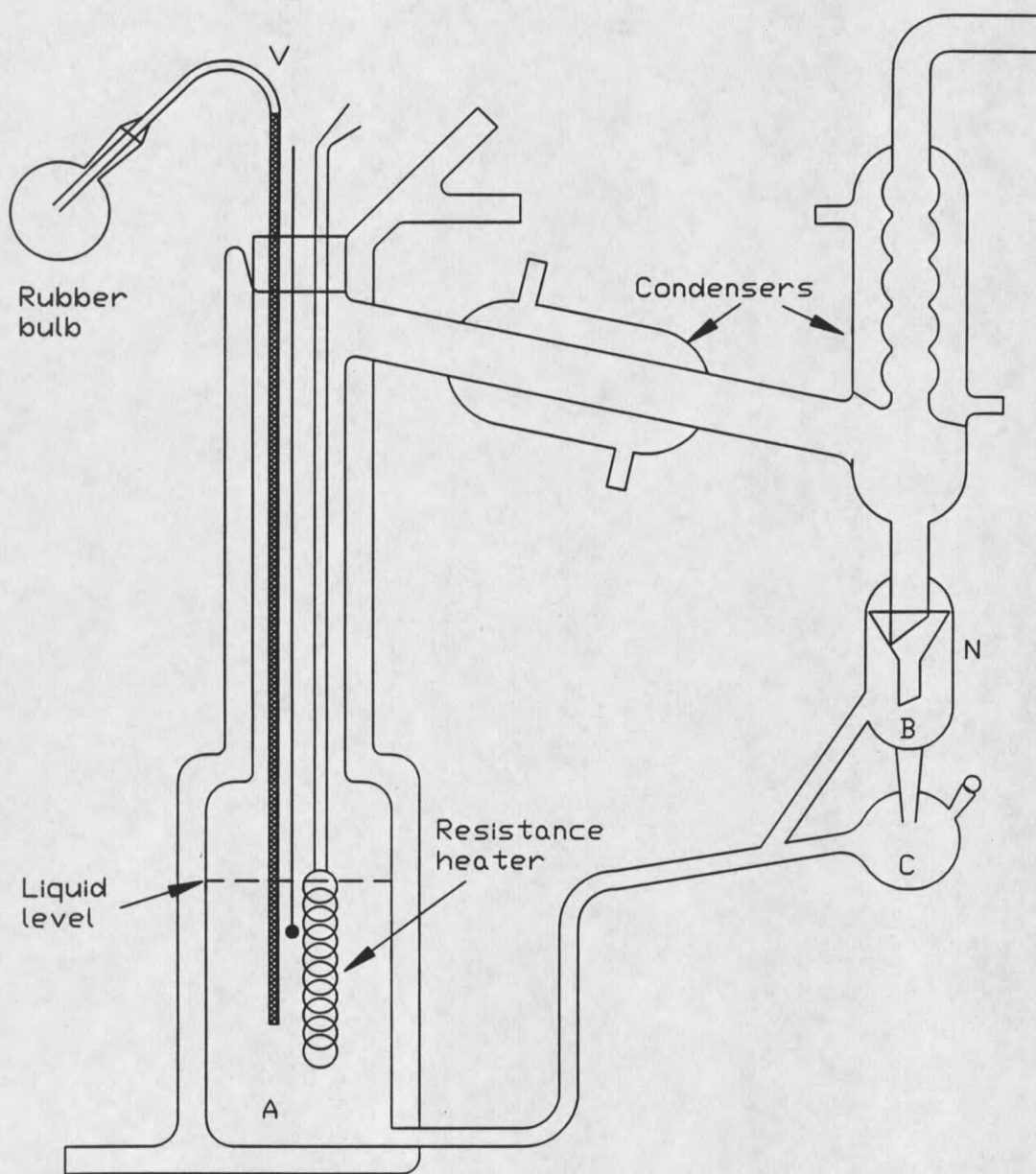


Figure 5: Kortüm VLE still [3].

The Jones still, shown in Figure 6 [3], is a fairly uncomplicated design. The liquid chamber A is heated by electrical wire wrapped around the vessel. This heating continues to the start of the condenser, where vapors are cooled for collection in receiver B. The condensate is completely vaporized in section V by electrical wire wrapped around the glass tube. The vaporized condensate is then returned to the liquid chamber where it is bubbled through the liquid sample. The bubbling vapor provides the only mixing in this chamber. This design yields very precise results [3], and is easily constructed. However, operation of this still can be difficult. Heating rates must be adjusted such that sufficient vapor circulates to ensure adequate mixing, while keeping this circulation below the maximum capacity of the vaporizer (V). Exceeding this capacity results in liquid holdup in the vapor return line.

Figure 7 illustrates the Williams still [3], a specialized design for use at low pressures (0.1 to 1 mmHg). In this design, liquid is heated in vessel A, which is insulated to reduce heat loss. The vapors are condensed and collected in tube B. The desired pressure is measured and maintained through the opening at M. The accuracy of this still is reported to be quite good [3]. Disadvantages of this design include the lack of any stirring mechanism in vessel A, the lack of any temperature measurement, and the absence of any method for liquid sampling.

The final still design discussed here is the Fowler-Norris still (Figure 8) [3]. Liquid is boiled in chamber A with an internal heater H, and a mixture of the liquid and vapor rises through P. From P, the mixture enters the equilibrium chamber R. The mix-

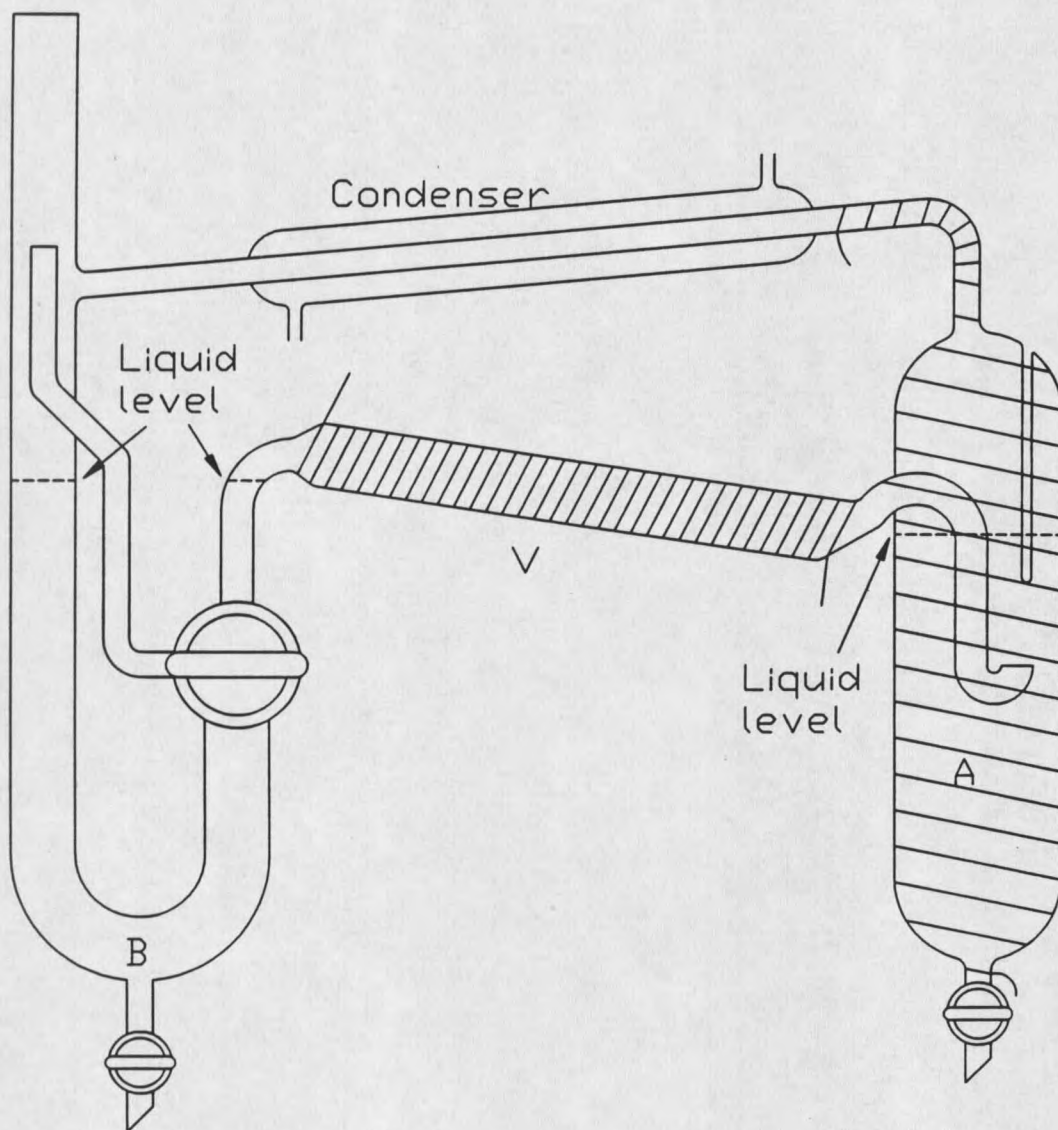


Figure 6: Jones VLE still [3].

