EXPERIMENT 14 Binary Liquid-Vapor Phase Diagram

This experiment is concerned with the heterogeneous equilibrium between two phases in a system of two components. The particular system to be studied is acetone-chloroform at 1 atm pressure. This system exhibits a strong negative deviation from Raoult’s law resulting in the existence of a maximum boiling point.

THEORY
For a system of two components (A and B), we have from the phase rule, \( F = C - P + 2 = 4 - P \) (1)

where C is the number of components (minimum number of chemical constituents necessary to define the composition of every phase in the system at equilibrium), P is the number of phases (number of physically differentiable parts of the system at equilibrium), and F is the variance or number of degrees of freedom (number of intensive variables pertaining to the system that can be independently varied at equilibrium without altering the number or kinds of phases present).

When a single phase is present, the pressure \( p \), the temperature \( T \), and the composition \( X_B \) (mole fraction of component B) of that phase can be varied independently; thus a single-phase two-component system at equilibrium is defined, except for its size, by a point in a three-dimensional plot in which the coordinates are the intensive variables \( P \), \( T \) and \( X_B \) (see Fig. 1). When two phases, e.g., liquid L and vapor V are present at equilibrium, there are four variables, but only two of them can be independently varied. Thus, if \( P \) and \( T \) are specified, \( X_{BL}^o \) and \( X_{BV}^o \) (the mole fractions of B in L and V) are fixed at their limiting values (\( X_{BL}^o \) and \( X_{BV}^o \)) for the respective phases at this \( P \) and \( T \). The loci of points \( X_{BL}^o (P, T) \) and \( X_{BV}^o (P, T) \) constituting two surfaces, shown in Fig. 1. The shaded region between them may be interpreted as representing the coexistence of two phases L and V if in this region \( X_B \) is interpreted as a mole fraction of B for the system as a whole. Within the two-phase region, \( X_B \) is not to be regarded as one of the intensive variables constituting the variance (although in a single-phase region it is indeed one of these variables). In a two-phase region the value of \( X_B \) determines the relative proportions of the two phases in the system; as \( X_B \) varies from \( X_{BL}^o \) to \( X_{BV}^o \) the molar proportion \( x_V \) of vapor phase varies from zero to unity:

\[
x_V = 1 - x_L = \frac{X_B - X_{BL}^o}{X_{BV}^o - X_{BL}^o}
\] (2)

Figure 1 is drawn for the special case of two components that form a complete range of ideal solutions, i.e. solutions that obey Raoult’s law with respect to both components at all compositions. According to this law, the vapor pressure (or partial pressure in the vapor) of a component at a given temperature \( T_1 \) is proportional to its mole fraction in the liquid. Thus in Fig. 1 the light dashed lines representing the partial pressures \( P_A \) and \( P_B \) and the total vapor-pressure line (L, joining \( P_A^0 \) and \( P_B^0 \)) are straight lines when plotted against the liquid composition. However, the total vapor pressure as plotted against the vapor composition is not linear. The curved line \( V \), joining \( P_A^0 \) and \( P_B^0 \), is convex downward, lying below the straight line on the constant-temperature section: its slope has everywhere the same sign as the slope of L.

* The complete definition of the system would of course include also its shape, description of surfaces, specification of fields, etc.: ordinarily these have negligible effects as far as our present discussion is concerned.
The vapor pressures $P^0_A$ and $P^0_B$ of the pure liquids increase with temperature (in accord with the Clapeyron equation) as indicated by the curves joining $P^0_A$ with $P'_0A$ and $P^0_B$ with $P'_0B$. At a constant pressure, say 1 atm, the boiling points of the pure liquids are indicated as $T^0_A$ and $T^0_B$.

The boiling point of the solution, as a function of $X_{BL}$ or $X_{BV}$ is represented by the curve $L^*$ or $V^*$ joining these two points. Neither curve is in general a straight line. If Raoult's law is obeyed, both are convex upward in temperature, the vapor curve lying above the liquid curve in temperature and being the more convex.

In most binary liquid-vapor systems, Raoult's law is a good approximation for a component only when its mole fraction is close to unity. Large deviations from this law are commonplace for the dilute component or for both components when the mole fraction of neither is close to unity. If at a given temperature the vapor pressure of a solution is higher than that predicted by Raoult's law, the system is said to show a positive deviation from that law. For such a system, the boiling-point curve $L^*$ at constant pressure is usually convex downward in temperature. If at a given temperature the vapor pressure of the solution is lower than that predicted by Raoult's law, the system is said to show a negative deviation; in this case the curve $L^*$ is more convex upward. These deviations from Raoult's law are often ascribed to differences between "heterogeneous" molecular attractions (A-B) and "homogeneous" attractions (A-A and B-B). Thus the existence of a positive deviation implies that homogeneous attractions are stronger than heterogeneous attractions, and a negative deviation implies the reverse. This interpretation is consistent with the fact that positive deviations are usually associated with positive heats of mixing and volume expansions on mixing, while negative deviations are usually associated with negative heats and volume contractions.

In many cases the deviations are large enough to result in maxima or minima in the vapor-pressure and boiling-point curves. as shown in Fig. 2. Systems for which the boiling-point curves have a maximum include acetone-chloroform and hydrogen chloride-water; systems with a minimum include methanol-chloroform, water-ethanol, and benzene-ethanol. At a maximum or a minimum, the compositions of the liquid and of the vapor are the same: accordingly, there is a point of tangency, of the curves $L$ and $V$ and of the curves $L^*$ and $V^*$ at the maximum or minimum. At every value of $X_B$, the slope of $V$ (or $V^*$) has the same sign as the slope of $L$ (or $L^*$); one is zero where and only where the other is zero, at the point of tangency. (A common error in curves of this kind, found even in some textbooks, is to draw a cusp-a point of discontinuity of slope-in one or both curves at the point of tangency: both curves are in fact smooth and have continuous derivatives.)

If the homogeneous attractions are very much stronger than the heterogeneous ones, phase separation may occur in the liquid; i.e., there is a limited mutual solubility of the two liquid components over certain pressure and temperature ranges. If the pressures and temperatures at which two liquid phases coexist include those at which equilibrium also exists with the vapor phase, a boiling-point diagram of a type similar to that shown in Fig. 15-1 is found. (That figure is a melting-point diagram, showing two solid phases in equilibrium with a liquid phase, but the principles are the same. It will be noted that boundaries of fields show discontinuities in slope at points representing the coexistence of three phases.)
Liquid-vapor phase diagrams and boiling-point diagrams in particular, are of importance in connection with distillation, which usually has as its object the partial or complete separation of a liquid solution into its components. Distillation consists basically of boiling the solution and condensing the vapor into a separate receiver. A simple 'one-plate' distillation of a binary system having no maximum or minimum in its boiling-point curve can be understood by reference to Fig. 3. Let the mole fraction of B in the initial solution be represented by $X_{BL1}$. When this is boiled and a small portion of the vapor is condensed, a drop of distillate is obtained, with mole fraction $X_{BV1}$. Since this is richer in A than is the residue in the flask, the residue becomes slightly richer in B, as represented by $X_{BL2}$. The next drop of distillate $X_{BV2}$ is richer in B than was the first drop. If the distillation is continued until the entire residue has boiled away, the last drop to condense will be virtually pure B. To obtain a substantially complete separation of the solution into pure A and B by distillations of this kind, it is necessary to separate the distillate into portions by changing the receiver during the distillation, then subsequently to distill the separate portions in the same way and so on, a very large number of successive distillations being required. The same result can be achieved in a single distillation by use of a fractionating column containing a large number of "plates"; discussion of the operation of such a column is beyond the scope of this book. If there is a maximum in the boiling-point curve (Fig. 2b), the compositions of vapor and residue do not approach pure A or pure B but rather the composition corresponding to the maximum. A mixture with this composition will distill without change in composition and is known as a constant-boiling mixture or...
Azeotrope. These terms are also applied to a mixture with a minimum boiling point. Azeotropes are important in chemical technology. Occasionally they are useful (as in constant-boiling aqueous hydrochloric acid, used as an analytical standard); often they are nuisances (as in the case of the azeotrope of 95 percent ethanol with 5 percent water: the existence of which prevents preparation of absolute ethanol by direct distillation of dilute solutions of ethanol in water). Extensive lists of azeotropes have been compiled. 

METHOD

A boiling-point curve can be constructed from data obtained in actual distillations in an ordinary “one-plate” distilling apparatus. Small samples of the distillate are taken directly from the condenser, after which small samples of the residue are withdrawn with a pipette. The samples of distillate and residue are analyzed, and their compositions are plotted on a boiling-point diagram against the temperatures at which they were taken. In the case of the distillate, the temperature to be plotted for each sample should be an average of the initial and final values during the taking of the sample. In the case of the residue, the temperature to be plotted should be that recorded at the point where the distillation is stopped to take the sample of residue.

For analysis of the samples, a physical method is often preferable to chemical methods. Chemical analysis usually is appropriate only when a simple titration of each sample is involved, as in the case of the system HCl-H₂O. If a physical property is chosen as the basis for an analytical method, it should be one that changes significantly and smoothly over the entire composition range to be studied. The refractive index is one property that can be used, as it is almost a linear function of the weight percent of a component. Pure acetone has a refractive index of 1.4171 and chloroform has a refractive index of 1.4459.

Another property that could also be used is the density, which varies in a nonlinear way between 0.7899 g/mL for acetone and 1.4832 g/mL for chloroform at 20°C. In this case, a calibration curve should be constructed from known solutions or provided by the instructor. The density of each distillation sample can be measured by pipetting 1 mL into a small, previously weighed vial and then weighing again (to the nearest 0.1 mg).

Warning: Do not inhale the vapor while taking samples.

EXPERIMENTAL

The thermometer bulb should be about level with the side arm to the condenser so that the temperature of coexisting vapor and liquid is measured. Except when samples of distillate are being taken for analysis, an adequate receiving flask should be placed at the lower end of the condenser.

Before beginning the distillations, prepare twenty 5-mL vials for taking samples and label with the designations IL, 1V, 2L, … , 10V (L = liquid residue; V = condensed vapor or distillate). Take samples of about 2 mL in size. Turn on the circulating water to the condenser before heating the liquid and turn it off at the end of the experiment.

When the distillation is proceeding at a normal (not excessive) rate at about the desired temperature, quickly replace the receiver with a vial and read the thermometer. After about 2 mL has been collected, read the thermometer again, replace the receiver, and seal the vial tightly. Turn off and lower the heating mantle to halt the distillation. When the temperature just begins to fall, record
another thermometer reading. After the flask has cooled about 15°C, remove the glass plug on the side arm of the flask and insert a 2-mL pipette equipped with a rubber bulb. Fill the pipette, discharge it into the appropriate vial, and stopper the vial.

![Image](image.png)

The following procedure for cyclohexanone/tetrachloroethane is recommended for economical use of materials in carrying out this experiment. Use a similar procedure for chloroform/acetone; with different temperatures and compositions than the ones indicated. The paragraph numbers correspond to sample numbers. A graduated cylinder is adequate for measuring liquids. The temperatures recommended are those appropriate for 760 Torr; at ambient pressure differing markedly from this value, the temperatures should be adjusted accordingly. For example at Denver (altitude 1609 m) the average atmospheric pressure is 836 mbar = 627 Torr. Since the enthalpies of vaporization of cyclohexanone and tetrachloroethane are both near 40 kJ mol⁻¹, this pressure change will reduce the boiling points of the pure materials by ~7°C compared with the values at 760 Torr. Comparable changes are expected for the azeotrope and for intermediate compositions.

1. Pure tetrachloroethane: Introduce 125 mL (~200 g) of 1,1',2,2'-tetrachloroethane into the flask. Distill enough to give a constant temperature (should be near 146°C at 760 Torr). Collect samples (1V and 1L) for analysis.
2. 149°C (tetrachloroethane-rich side of azeotrope): Cool the distilling flask and return the excess distillate of paragraph 1 to the flask. Add 38 mL (~36 g) of cyclohexanone. Begin distillation. When the temperature reaches 149°C, collect about 2 mL of distillate (2V) and 2 mL of residue (2L).
3. 151°C: Resume the distillation. Distill until the temperature reaches 151 °C (this may take some time) and collect samples (3V & 3L).
4. 154 °C: Resume the distillation. When the temperature reaches 154 °C collect samples (4V & 4L).
5. 157°C: Cool the flask somewhat and add 35 mL of tetrachloroethane and 25 mL of cyclohexanone. Resume the distillation. When the temperatures reaches approximately 157 °C collect samples (5V & 5L).
6. Azeotrope: Cool the flask somewhat and add 36 mL of tetrachloroethane and 54 mL of cyclohexanone. Resume the distillation until the boiling point ceases to change significantly and take samples (6V & 6L). (If the boiling point does not become sufficiently constant. Analyze the remaining residue and make up 100 mL of solution to the composition found. Distill to constant temperature and take samples.)
7. Pure cyclohexanone: Introduce 105 mL of cyclohexanone into the clean flask and determine the boiling point as in paragraph 1. (The temperature should be near 155 °C at 760 Torr). Collect samples (7V and 7 L).
8. 156.5°C (cyclohexanone-rich side of azeotrope): Cool the distilling flask, return the excess distillate of paragraph 7 and add 20 mL of tetrachloroethane. Resume the distillation, and take samples (8V & 8L) at about 156.5°C.
9. 157°C: Cool the flask somewhat and add 50 mL cyclohexanone and 17 mL tetrachloroethane. Resume the distillation and collect samples (9V & 9L) at about 157°C.
10. Azeotrope: Resume the distillation, continue to constant boiling temperature, and take samples (10V & 10L).

The indexes of refraction should be measured and recorded as soon as possible. If careful attention is given to the proper technique of using the refractometer, it should be possible to take readings at the rate of one sample per minute.

At some time during the laboratory period, the barometer should be read. The ambient temperature should be recorded for the purpose of making thermometer stem corrections if these are necessary.

**CALCULATIONS**
Determine the weight-percent compositions from the refractometer data and then convert the weight percentages to mole fractions. Plot the temperatures (after making any necessary stem corrections) against the mole fractions. Draw one smooth curve through the distillate points V and another through the residue points L. Label all fields of the diagram to indicate what phases are present. Report the azeotropic composition and temperature, together with the atmospheric pressure (i.e., the properly corrected barometer reading).

**SAFETY ISSUES**
Do not pipette any chemical by mouth, and avoid inhaling the vapor while withdrawing samples. Dispose of waste chemicals as instructed.

**REFERENCES**