

Investigating the Liquid-Vapor Transition

Background

In the liquid phase matter conforms to the shape of its container but remains fluid, subject to external forces which can cause the unmistakable sloshing behavior we associate with ordinary liquids like water in a bucket. Still, there is cohesion among the particles that make up the liquid, some kind of binding force that keeps individual particles from each going their own way as happens in a gas. Water spilled from a bucket makes a puddle, it does not disappear immediately into the air. Even liquid mercury--with its unusual behaviors--still displays a kind of cohesion, although puddles of the molten metal may easily be divided into smaller, separate parts.

The forces which operate between particles of liquids are in the category we often call *weak forces*. The same kinds of attractions are responsible for holding together molecular solids: hydrogen bonding, dipole forces, dispersion forces. The difference is twofold: in liquids the particles are marginally farther apart *and* they possess more kinetic energy than in the corresponding solid state. These differences work together to give liquids their combination of fluidity and cohesion. However, common experience shows that while water spilled from a bucket does not immediately vaporize into thin air, it will eventually do exactly that.

Particles within the liquid are in constant motion due to their thermal energy. They collide with each other and with the container walls--except at the surface. There, unbalanced forces act on the particles as there is no liquid immediately above, only the air. Although the particles as a group have the same *average* kinetic energy, that average is made of many different values, some high enough to overcome the weak forces which bind the liquid together. If these particles are on the surface and a collision imparts the correct momentum, they can leave the liquid altogether (vaporization). This single example, multiplied many times over, is what evaporation is all about.

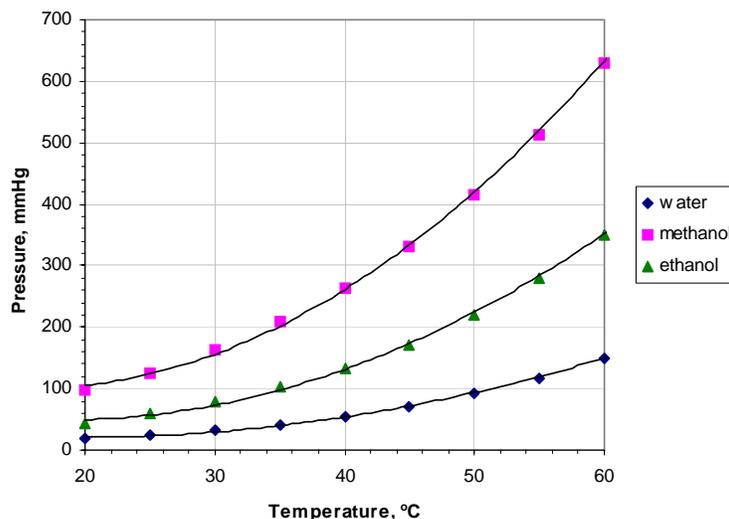
If we now extend this scenario to a *closed* container (not completely full of liquid), there is nothing to stop the same thing from happening. However, the particles which escape from the liquid surface are trapped in the space above the liquid. Although in the gas phase, these particles too are subject to many collisions with the container walls and cover as well as--much less often--molecules of the gases in air that are trapped with them. They too have an *average* kinetic energy based on the ambient temperature and some of those kinetic energies will be low enough that collision with the surface of the liquid may result in capture (condensation) due to the weak forces.

Over time these two processes reach the same rate (assuming the temperature is held constant). A device for measuring gas pressure would show more than atmospheric pressure in such a container. The additional pressure is from the equilibrium portion of particles which have escaped the liquid. This is what is called *vapor pressure*.

Vapor pressure is related to the strength of the weak forces as well as the temperature but not to the exposed surface area or the volume of the space above the liquid (assuming there is not so much space that all of the liquid evaporates before equilibrium can be established). These other factors may influence the *rate* at which vapor pressure equilibrium is achieved, but the ultimate result will be the same for a given liquid at a given temperature. The amount of vapor pressure generated is thus tied to the energy needed to overcome the forces which hold the liquid together.

Adapted from A Simple Experiment for Determining Vapor Pressure and Enthalpy of Vaporization of Water, Gerald S. Levinson, *J. Chem Ed.*, vol. 59, No. 4, p. 337

Vapor pressure vs. temperature



Experiment shows that vapor pressure is not a linear function of temperature but has instead a more complicated logarithmic relationship.

Since the application of heat can both increase vapor pressure and also eventually cause a liquid to boil [at this point the vapor pressure of the liquid equals the prevailing atmospheric pressure] it might not be surprising that there is a relationship between vapor pressure and the *heat of vaporization* of a liquid. The heat of vaporization, ΔH_{vap} , is the heat needed to change the liquid to a gas. Linearizing the vapor pressure/temperature relationship results in a type of function which appears frequently in chemistry:

$$\ln P = - \frac{\Delta H_{\text{vap}}}{RT} + C$$

where **P** is the vapor pressure at temperature **T** (in kelvins) and **R** is 8.31 J/mol·K [the units for the heat of vaporization must be consistent with these others]. The constant, **C**, has no special significance in this discussion and it could be eliminated by writing this expression in a different form. In its current form, however, it should be noted that this is an equation for a line in slope-intercept form:

$$\ln P = - \frac{\Delta H_{\text{vap}}}{R} \frac{1}{T} + C$$

$$y = m x + b$$

Thus, if the vapor pressure of a liquid can be measured at several different temperatures, a plot of $\ln P$ vs. $1/T$ will yield a straight line from which the heat of vaporization may be determined. Although inspection of this relationship might lead one to question what the "correct" units for the vapor pressure should be, in reality it does not matter. If the relationship is rewritten in point-slope form that should be evident:

$$\ln P_2 - \ln P_1 = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

The units of the pressure will cancel, whatever they may be.

This form of the equation is known as the *Clausius-Clapeyron equation* and it appears in various contexts including the determination of activation energies or rate constants, estimating equilibrium constants at different temperatures, and more. In each context it has limitations. For vapor pressures and heats of vaporization it begins to break down near the critical point of a liquid and at very high pressures. Chemical engineers often use a different relationship known as the *Antoine equation*:

$$\log P = A - \frac{B}{T + C}$$

where **T** is temperature and **A**, **B**, and **C** are *Antoine coefficients* that can be found in reference tables. Each substance has its own coefficients and they are generally only valid for particular temperature ranges. The numbers are derived from curve-fitting experimental data. Values of coefficients vary from table to table because many different units are used so it is important to look carefully before calculating away blindly with numbers. [the vapor pressure graph for water, methanol and ethanol shown earlier was plotted using the Antoine equation]

So far the discussion has focused on pure liquids. Mixtures of miscible liquids (i.e., solutions) cannot be so easily described because of the various interactions which may occur between the molecules. Assuming that these interactions are physical and not chemical, solution types may be roughly divided into two groups: those containing non-volatile solutes and those containing volatile solutes.

When a non-volatile solute is dissolved in a liquid, e.g., glycerol in water, the entropy of the mixture is higher than the entropy of either the pure solvent or solute. Because the solute has no appreciable vapor pressure of its own, only solvent molecules make the transition to the vapor phase in the manner described earlier. The energy required for this process is no different since it is, in fact, the same process.

There *is*, however, a difference in the entropy change. Since the end is the same (some solvent molecules in the gas phase) but the beginning state has greater entropy (the mixture) the overall change in entropy (ΔS) for the vaporization of the solution is smaller than for the pure solvent. The net effect of this difference is to require a higher temperature to reach vapor pressure equilibrium since:

$$\text{at equilibrium } \Delta G = 0 = \Delta H - T\Delta S$$

← stays constant
↑ must increase
← gets smaller

This difference is, of course, the basis for the colligative properties known as *vapor pressure lowering* and *boiling point elevation* (which is a direct result of the former). The theoretical vapor pressure of a solution is determined as if the components of the solution were independent and each contributed a portion of the total vapor pressure according to their concentration as mole fractions of the mixture:

$$P_{\text{soln}} = \chi_1 P_1^{\circ} + \chi_2 P_2^{\circ}$$

where χ_i is the mole fraction of a component (here, the solute is component 1) and P_i° is the vapor pressure of the pure substance at whatever the temperature is. More simply, since $P_1^{\circ} = 0$:

$$P_{\text{soln}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

This statement is known as *Raoult's Law*.

As is the case with all of the expressions used to describe the colligative properties, this is a simplification of an often more complex situation. While the solute may indeed have a negligible vapor pressure it will most likely interact with the solvent in some way or a solution would not form in the first place. Solute-solvent interactions (and even interactions among like molecules) can produce surprising deviations from the simple behavior predicted by Raoult's Law, especially at higher concentrations.

The second type of solution is made of components which are both volatile ["both" is a simple approximation; solutions may have more than two components]. The behavior here is more complex but can be approached with the principles already described. Both solute and solvent have their own tendencies to vaporize at a given temperature. If we extend Raoult's Law to this situation we can think of a mixture of two liquids which will have their own "partial pressures" based on their vapor pressures and the proportion of them present. Blending *Dalton's Law of Partial Pressures* into the mix we get:

$$P_{\text{soln}} = P_1 + P_2 \quad [\text{statement of partial pressures in the vapor phase}]$$

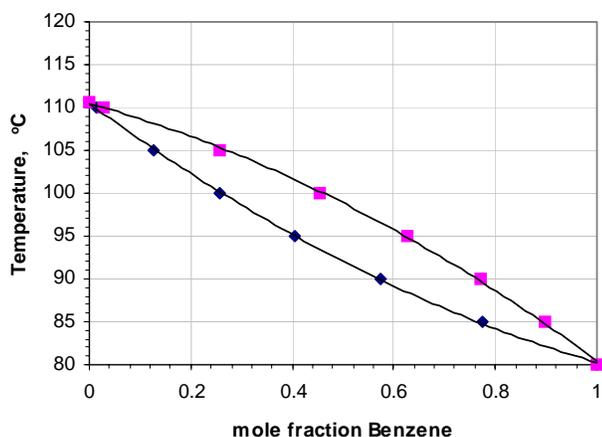
$$P_{\text{soln}} = \chi_1 P_1^{\circ} + \chi_2 P_2^{\circ} \quad [\text{Raoult's Law for volatile solutes}]$$

Of course, this is the same expression as written originally. The difference is that $P_{\text{solute}}^{\circ}$ (i.e., P_1°) is not zero in this case.

If the simple one-component volatile system is idealized in Raoult's Law, the binary system is even more so. In an "ideal" solution the intermolecular forces among all of the molecules would be the same. This is most closely approximated by adjacent compounds in homologous series such as pentane and hexane, or ethanol and propanol, etc. *The hallmarks of such mixtures include a zero-value enthalpy of mixing as well as a zero-value volume change on mixing.* Deviations are common enough, however, that at least two categories merit mentioning. Mixtures will have a *positive deviation* from Raoult's Law (i.e., the measured vapor pressure will be greater than that calculated by the simple form of the law shown above) if the forces between unlike molecules are weaker than the forces among the two pure component molecules. It is therefore easier for particles to escape the liquid. *Negative deviations* are seen when there is a strong interaction between the two components. Then the vapor pressure of the mixture is lower than expected.

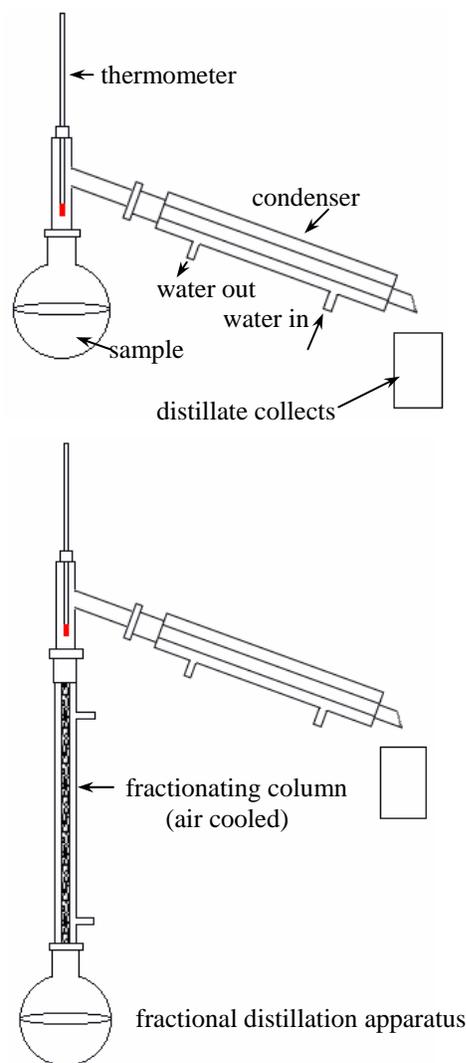
Simple distillation is a common way to separate volatile and non-volatile solution components (such as salt and water) but because of the way in which the two vapor pressures in a binary mixture of volatile components combine, distillation of such mixtures with a goal of separating the components is difficult, at best. For any kind of reasonable separation the boiling points must be (at least) approximately 25°C apart. Even then, the initial distillate collected will contain the highest proportion of the lower-boiling component and the final distillate collected will contain the highest proportion of the higher-boiling component. Between these two extremes the composition of the distillate changes gradually (in a nearly ideal mixture) as represented in the diagram on the following page.

Liquid-Vapor Phase Diagram for Benzene-Toluene System

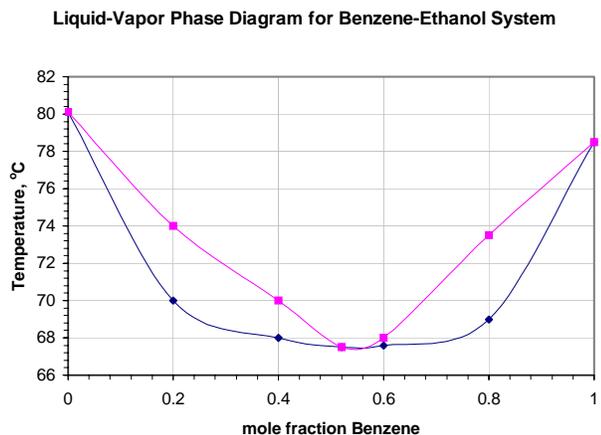
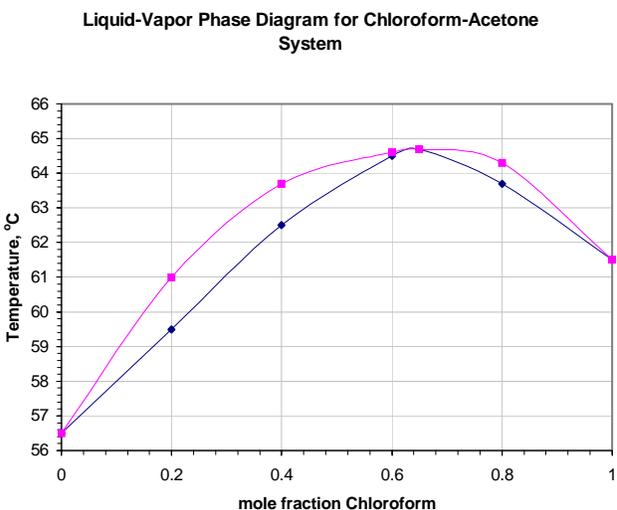


The diagram shows a common form of binary liquid-vapor phase diagram. The upper curve represents the changing composition of the vapor phase and is sometimes called the *dew point curve*. The lower curve is for the liquid phase and is sometimes known as the *bubble point curve*. The mole fraction of only one component is represented on the x-axis (since the sums of the mole fractions are always 1). Choosing a temperature on the y-axis, it is possible to determine the composition of the vapor and liquid phases at equilibrium (reflux-boiling). Clearly only the extremes of the simple distillation process give reasonably pure fractions of the mixture components.

To increase the efficiency of the distillation of mixtures like this a different process called *fractional distillation* is used. The effect (not the technique) of fractional distillation is to redistill various fractions along the continuum of possibilities, each time obtaining a better separation because the new mixture begins richer in one component than the other. As a practical matter this would be extremely tedious. In practice, a *fractionating column* is added to the typical simple distillation set-up. Along this column there is a significant temperature gradient and a tortured path for the vapor which allows for many condensation points along the gradient. As the mixture is heated and the vapors rise into the fractionating column the lower-boiling component vapor gradually works its way to the top of the column (where it is coolest) and eventually enters the simple distillation condenser. Meanwhile the higher-boiling component is condensing in the cooler areas of the fractionating column and dripping back into the distillation flask. Gradually the residue becomes poorer in the lower-boiling component and richer in the higher-boiling component. Very efficient columns with many "plates" or condensation points/gradients can achieve excellent separations of many mixtures.



Some non-ideal solutions show marked variation from the simple behavior already described and cannot be completely separated even by fractional distillation. They tend to form mixtures during distillation which behave like pure substances, boiling at a constant temperature. Such mixtures are called *azeotropes*. Large negative deviations from Raoult's Law can result in maximum-boiling azeotropes while large positive deviations can yield minimum-boiling azeotropes:



It is possible to construct binary liquid-vapor phase diagrams from theoretical calculations (assuming ideal behavior--NO azeotropes). The derivation of the expressions for the dew point and bubble point curves is based on Raoult's and Dalton's Laws:

$P_1 + P_2 = P_T$	$= \chi_1 P_1^o + \chi_2 P_2^o$
Dalton's Law of Partial Pressures	Raoult's Law

where χ_1 represents the mole fraction of the lower-boiling component in the liquid phase at a given temperature. Since the mole fractions combined must be 1, the expression can be rewritten in that single variable:

$$P_T = \chi_1 P_1^o + (1 - \chi_1) P_2^o$$

$$P_T = \chi_1 P_1^o + P_2^o - \chi_1 P_2^o$$

$$P_T = P_2^o + \chi_1 (P_1^o - P_2^o)$$

Solving this expression for χ_1 we have the bubble point equation:

$$\chi_{1(l)} = \frac{P_T - P_2^o}{P_1^o - P_2^o}$$

This gives the lower line in the liquid-vapor phase diagram. P_T is typically taken as 760 mmHg or the equivalent.

The derivation for the dew point equation is more complex and includes the use of the Dalton's Law part of the equation as well. Since $P_1 = \chi_{1(g)}P_T$ (where P_1 is the partial pressure of the vapor of component 1 in the total gas phase) and also $P_1 = \chi_{1(l)}P_1^o$ then

$$\chi_{1(g)} = \frac{\chi_{1(l)}P_1^o}{P_T}$$

If the bubble point equation is now substituted for $\chi_{1(l)}$ the following expression is obtained:

$$\chi_{1(g)} = \frac{P_1^o[(P_T - P_2^o)/(P_1^o - P_2^o)]}{P_T}$$

OR

$$\chi_{1(g)} = \frac{P_1^o(P_T - P_2^o)}{P_T(P_1^o - P_2^o)}$$

This gives the upper or vapor line in the binary liquid-vapor diagram (again, P_T is generally taken to be 760 mmHg).

There are several ways to judge the ideal behavior of a mixture (in addition to measuring enthalpy of mixing and volume change on mixing). If the mixture conforms well to Raoult's Law then it can be considered ideal. One way to test that is to measure the vapor pressure of a mixture and use the data to calculate the molar mass of the solute. If there is good agreement with the known molar mass then Raoult's Law describes the behavior of the mixture reasonably well.

The connection between the vapor pressure of the mixture and the molar mass of the solute is not obvious and deserves a closer look. Raoult's Law for this situation has already been shown:

$$P_{\text{soln}} = \chi_{\text{solute}}P_{\text{solute}}^o + \chi_{\text{solvent}}P_{\text{solvent}}^o$$

We can rewrite this expression in terms of the mole fraction of the solvent *only* since $\chi_{\text{solute}} + \chi_{\text{solvent}} = 1$:

$$P_{\text{soln}} = (1 - \chi_{\text{solvent}})P_{\text{solute}}^o + \chi_{\text{solvent}}P_{\text{solvent}}^o$$

$$P_{\text{soln}} = P_{\text{solute}}^o - \chi_{\text{solvent}}P_{\text{solute}}^o + \chi_{\text{solvent}}P_{\text{solvent}}^o$$

$$P_{\text{soln}} = P_{\text{solute}}^o + \chi_{\text{solvent}}(P_{\text{solvent}}^o - P_{\text{solute}}^o)$$

$$\chi_{\text{solvent}} = \frac{P_{\text{soln}} - P_{\text{solute}}^o}{P_{\text{solvent}}^o - P_{\text{solute}}^o} \quad [1]$$

But χ_{solvent} may also be written in terms of the moles of the components:

$$\chi_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{solute}}}$$

If this expression is multiplied by the (molar mass of the solvent/molar mass of the solvent) we then have:

$$\chi_{\text{solvent}} = \frac{\text{MM}_{\text{solvent}} n_{\text{solvent}}}{\text{MM}_{\text{solvent}} (n_{\text{solvent}} + n_{\text{solute}})} = \frac{\text{MM}_{\text{solvent}} n_{\text{solvent}}}{\text{MM}_{\text{solvent}} n_{\text{solvent}} + g_{\text{solute}}}$$

when this expression is substituted into equation [1] it is possible to isolate $\text{MM}_{\text{solute}}$:

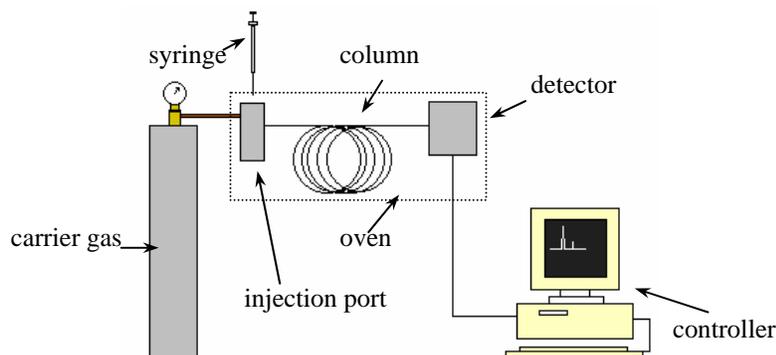
$$\text{MM}_{\text{solute}} = \frac{g_{\text{solute}}}{n_{\text{solvent}}} \left(\frac{P^{\circ}_{\text{solute}} - P^{\circ}_{\text{solvent}}}{(P_{\text{soln}} - P^{\circ}_{\text{solvent}})} - 1 \right)$$

Thus knowing the composition of the mixture (moles of solvent, gram of solute) and the vapor pressures of the pure components and the mixture at a given temperature it is possible to calculate the molar mass of the solute.

An ideal or nearly ideal mixture will also have a liquid-vapor phase diagram that conforms closely to that predicted by calculation. It is possible to construct such a diagram by experiment. A careful simple distillation of the mixture can be done to obtain fractions of condensed vapor over small temperature ranges. If these fractions are analyzed they can yield the data at the average collection temperatures for a dew point curve. If the fractions are large enough to make it practical, boiling points can also be determined for the samples and that would supply the data for the bubble point curve. If the fractions are too small or have been compromised by long standing (the more volatile component leaves the sample gradually) then mixtures in various proportions can be prepared for boiling point measurements.

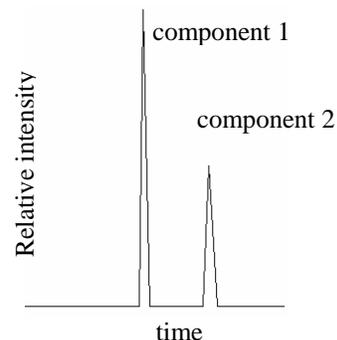
The analysis of the recovered vapor fractions could theoretically be done in several ways. Perhaps one of the simplest is to prepare known mixtures and measure their *index of refraction*, establishing a calibration curve. The index of refraction is the ratio of the speed of light in a vacuum to the speed of light through a substance. That sounds complicated but in practice a small sample is placed in a *refractometer* and a numerical reading is obtained. However, this is not a good method to use for closely related compounds such as near neighbors in homologous series like heptane and octane since their refractive indices are so similar that accurate measurement is extremely difficult if not impossible.

For small samples of volatile materials it is difficult to find a better technique--where equipment is available--than *gas chromatography* (GC). The instrument operates on the same principles as other chromatographic separation methods. The mixture is adsorbed onto a stationary phase in a column. Some columns (such as the one in the instrument used in this experiment) are very fine capillaries of considerable length (30 m!) wound in a coil. Each component experiences different attractions for the stationary phase (generally due to polarity) and when the mobile phase (a carrier gas like helium or nitrogen) passes through the stationary phase each component is "washed out" at varying rates, thus effecting a separation. A simple block diagram of a basic gas chromatograph is shown below.



The compounds in the sample are detected as they emerge from the column and a graph is produced in which peaks correspond to the components of the mixture. The areas under these peaks are proportional to the amount of substance present.

There are several ways to determine the areas under the peaks. One of the simplest is to cut out the peaks (or a photocopy of them) and mass them on the analytical balance. The areas will be directly proportional to the masses and the masses therefore proportional to the moles of substance.



The areas may also be approximated by the 'half-height' method. The width of the peak is measured at its half-height. The product of this width and the height is then approximately the area under the curve. This method works best when the peaks are very symmetrical and wide enough to yield meaningful measurements.

Most modern gas chromatographs (including the one used in this experiment) can determine the areas under the chromatographic peaks electronically and produce a printed report for each sample.

The Experiment

There are seven parts to this experiment:

- determine the vapor pressure of octane at several temperatures
- determine the vapor pressure of heptane near 40°C
- determine the vapor pressure of a mixture of heptane and octane near 40°C
- measure the boiling points of both heptane and octane
- distill a mixture of heptane and octane, collecting fractions
- analyze distillation fractions by gas chromatography
- measure boiling points of distillation fractions

The following non-locker materials will be provided:

- 10 mL/0.1 mL graduated cylinders
- 15 x 125 mm test tubes
- 1 L (tall) beaker
- Micro Combo Still[®] w/heating block
- heptane
- octane
- 50/50 mixture of heptane and octane
- 6 x 50 mm test tubes and capillary tubes
- standard thermometers
- 4 sample vials
- hot plate
- known heptane/octane mixture

The Chemicals

Heptane (C_7H_{16}) is the next compound in the homologous series of alkanes to which hexane also belongs and its chemical properties are essentially the same. It is used as a standard in testing "knock" for gasoline engines. May be irritating to respiratory tract and narcotic in high concentrations.

Octane (C_8H_{18}) follows heptane in the alkane series. Isomers of octane are components of ordinary gasoline.

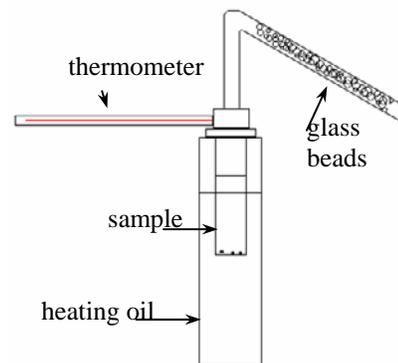
Technique Discussion

There are many things to be done in this experiment and it is not possible for every student to do the same sequence of steps simultaneously--especially where the gas chromatograph is concerned. It is convenient and (can be) efficient to work with a partner for this investigation. This simplifies data taking during the distillation, reduces demand for time on the chromatograph and allows for division of labor in repetitive tasks like boiling point determinations [it also provides a valuable chance to cross-check results from techniques that seem to be difficult].

Although the distillation is perhaps not the most obvious first step as the background material has been developed, logistically it is the best first step so that while one group is running samples through the chromatograph others may be working on vapor pressure measurements or boiling points.

On a traditional laboratory scale the distillation would be done using an apparatus such as pictured in the Background section for *simple distillation*. A lot of material is used in such a set-up (which has to be disposed of later) and the glassware is very expensive. The Micro Combo Still[®] addresses both of these issues and is also simpler to set up since it does not require running water for the condenser.

A 3 mL sample (50/50 composition) is provided in the small vial which forms the sample container for the apparatus. A few boiling stones should be added to prevent superheating and aid in smooth boiling. The apparatus is assembled as shown at the right and placed within the heating block on a hot plate. Although the condenser tube is not water-cooled the glass beads inside provide a tortured path for the distillate vapors and enough surface area for sufficient cooling to condense the vapor if the distillation rate is not too high. Labeled sample vials can be used to collect the four fractions (5°C range for each vial). It may be convenient to use blocks to bring the vials up to the end of the condenser tube so that they do not have to be held during the entire distillation.



The sample should be heated at a medium rate (start with setting "4" on the hotplate). The drops should not emerge faster than 1 per second. Too slow a rate will result in significant loss of the more volatile component and too fast a rate will make data very difficult to collect. The temperature should be recorded for each drop collected. The vials must be tightly capped immediately after a sample is complete.

The operation particulars for the gas chromatograph will be discussed in detail in class. What follows is a step-wise sequence for running the four samples. All data will be stored in the instrument to be printed out after class by the instructor. The Method for the sample analysis will be loaded into the computer before you begin and the oven and inlet temperatures set to decrease your wait time. Bring your samples to the GC and follow the steps given.

1. Press F2 to begin **Data Acquisition**.
 2. Press F5 to **Load Parameters**. Type in place of the parameter file shown:
PARAM:LVEQ.A
 3. Press F5 again to **Load** the actual parameter file. This is *very important*. If you simply press <Return> instead, the parameter file will not be loaded.
 4. Press F1 to **Prepare to Inject**.
 5. Type in the data file space:
DATA:LVIA.D (substitute your locker number for the 1 and change the letter "A" to B, C, etc. for subsequent samples)
Follow by <Return>. Please do not use any other kind of file names. These are the only kinds of files the instructor will look for when processing the data.
 6. Use TAB to move to the operator name field and type in your name and your partner's name.
 7. Wait for temperature equilibration and the message **Ready to Inject**.
 8. Use the "empty syringe" method to inject a sample of your mixture and start the run. Wait for run completion. [the instructor will demonstrate the injection method]
 9. Continue in this way (returning to F1, **Prepare to Inject**) until all your samples have been processed.
 10. Press F8 (Exit, Quit) twice. This should leave the instrument as you found it, ready for the next group.
-

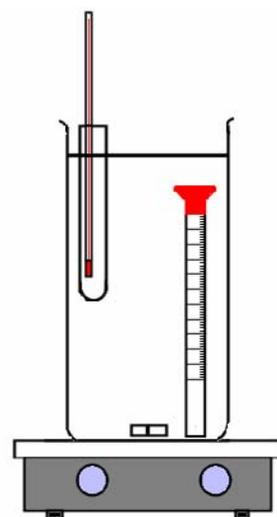
Determining the boiling point of a liquid sounds like a simple task and if the liquid is pure and there is unlimited sample available there *are* relatively simple methods. If the liquid is flammable and is not the kind of thing you want to breathe a lot then it is not a good idea to pour some into a beaker and heat it to boiling and check the temperature. Smaller scale methods are in order. The technique for measuring the boiling points of small samples of liquid is described in the **Introduction to the Laboratory**. Because the technique is not easy to master you should measure the boiling temperatures of the two pure liquids (which you can look up) to see if you are doing it correctly and to get used to the procedure.

Mixtures of volatile liquids require special skill because during boiling the more volatile component leaves the sample more quickly than the other substance. So the boiling point gradually rises. That means it is important to bring the liquid to a boil quickly and make the determination as soon as possible thereafter. Once a mixed sample has been boiled it cannot be reused. The boiling points of your distillation fractions should be measured to provide data for the bubble point curve. Discards should go into the container in the fume hood. Samples should be capped securely when not in use to prevent composition change--especially if GC analysis has not already been performed.

The determination of the vapor pressure of a liquid can be done in many ways. The classic method employs a mercury manometer and presents unacceptable risk. Modern experimental methods using *isoteniscope*s are complicated and require special glassware--and often a mercury manometer. In this experiment a small scale method is employed to measure the volume of an expanding vapor/air bubble at different temperatures. At constant pressure the volume can be used to calculate the total number of moles of gas. If the starting volume of air is known then the moles of air can be calculated and subtracted from the total, leaving the moles of vapor from the liquid. The partial pressure (which is the vapor pressure) can be calculated from this.

The apparatus consists of 10 mL graduated cylinder partially filled with water and then inverted in a 1 L beaker filled with water. A stirring bar is used to keep the water circulating and a thermometer is suspended in a test tube of the same water clamped in the beaker.

The cylinder is initially filled to approximately the 9 mL mark. When inverted this will trap an air bubble of approximately 3 mL volume. Ice is then added to the beaker to lower the temperature to near 0°C. At this temperature the vapor pressure of water is essentially negligible and the volume of the air bubble (along with the water temperature and room pressure) can be used to establish the moles of trapped air. A sample of the liquid for the vapor pressure measurements must next be introduced without adding to the air bubble. A Beral pipet with a stem bent into a hook is first filled ½ with the liquid and then water is added to the bulb until there is **no air** inside (including in the stem). The cylinder is carefully lifted partially out of the water and the liquid sample expelled into it. It is not necessary to expel all of the liquid mixture, but there must be enough of the alkane to form a separate layer in the cylinder.



Ice should then be removed from the beaker and replaced with slightly warm water until an equilibrium temperature of about 20°C is achieved. At this point the hot plate is turned on to a setting of “2” and the volume of the gas bubble (now air + alkane vapor + water vapor) is recorded every 5°C up to 50°C for the octane. For the heptane and the octane/heptane mixture only one reading is taken after the initial data: the volume of bubble at 40°C. These two samples may be run simultaneously in the same beaker if there are enough graduated cylinders available.

The critical technique is not heating too fast so that there is no lag between the temperature in the water bath and inside the cylinder itself. If the temperature is changing too fast the volume will be changing all the time and an accurate reading will be impossible.

This procedure involves several *constant determinate errors* which must be corrected when the data is analyzed. Reading the meniscus of such a narrow cylinder upside down is one of these. The pressure on the gas bubble in the cylinder is not exactly room pressure because the liquid levels inside and outside the cylinder cannot be equalized without affecting the temperature. Studies by the originators of the technique [for determining the vapor pressure of water] revealed that the volumes recorded are slightly high. Subtracting 0.2 mL from each recorded volume corrects reasonably well for these two problems.

When the technique is used to determine the vapor pressure of a water-insoluble liquid by introducing a layer on top of the water column—as in this experiment—a *proportional error* is introduced. Enough water clings to the sides of the cylinder where the bubble is to add the vapor pressure of water to the total pressure of the air bubble. Once the apparent vapor pressure of the alkane has been calculated for each temperature it must therefore be corrected by subtracting the vapor pressure of water at each temperature. These values can be found in the CRC Handbook or at NIST.

The Report

Your initial calculations should include:

[don't forget to adjust each volume recorded by subtracting 0.2 mL]

1. The moles of air in the cylinder at the ice-water temperature
2. The partial pressure of air in the cylinder at each temperature
3. The vapor pressure of octane at each temperature *[be sure to subtract the water vapor pressure!]*

[steps 1-3 should be repeated as needed for the vapor pressure of heptane and the mixture]

4. A plot of $\ln P$ vs. $1/T$ for your octane data *superimposed* on a similar plot of vapor pressure values from the Antoine equation [A, B, C available at NIST and in the CRC]
5. The heat of vaporization of octane from the graph of your data [relative error]
6. The extrapolated normal boiling point of octane from your data [relative error]
7. The molar mass of heptane based on the vapor pressure of the mixture of heptane and octane [relative error]
8. A liquid-vapor phase diagram for the heptane-octane system using your chromatograph data and the boiling points *superimposed* on a diagram plotted from Antoine vapor pressures and the ideal dew point/bubble point equations

Your conclusion to this experiment should include a brief comparison of your results with the calculated ideal results. For example, you measured the boiling point of octane and you also calculated it from your vapor pressure data. How well do these agree? Does the heat of vaporization agree better than the extrapolated boiling point? Attempt to explain why one value might be more accurate than the other. Account, if possible, for deviations in your phase diagram. Is one curve more accurate than the other? Why might this be?