

Determination of Activity Coefficients by Gas-Liquid Chromatography

Chromatography is a physical method for separating components of a mixture. In this technique a mixture is dissolved in a mobile phase, which is usually a gas or a liquid, then passed through a column that contains an immobile stationary phase, which is usually a liquid or a solid. The two phases are selected so that the solubilities of the components of a mixture are different in each phase. The different components in a mixture distribute themselves between the two phases and therefore pass through the column in different lengths of time. There are four different combinations of phases that can be used in a column, and thus four kinds of chromatography. With the mobile phase given first, they are: gas-liquid (GLC), gas-solid (GSC), liquid-liquid (LLC), and liquid-solid (LSC). This experiment involves the first kind, GLC. Using this method it is possible to separate a mixture of benzene, cyclohexane, and cyclohexene. From the chromatograph one can determine the retention times and volumes and use plate theory to determine the activity coefficients of each compound.

Figure 1 is a diagram of a gas chromatograph. A sample or solute is introduced into the instrument through a heated injector where it is vaporized and entrained by the mobile phase, or carrier gas. The mobile phase, and the sample it carries, is forced through a column where the separation occurs. The column is a metal or glass tube which contains an inert solid support to hold the liquid, stationary phase in the column. In a packed column, which is used in this experiment, the support usually consists of a porous material of finely granulated diatomaceous earth or clay. It absorbs the stationary phase on its surface in a thin, uniform film, with a loading capacity of up to 50% by weight. The stationary phase, or solvent, is a low vapor pressure liquid that is chosen for its specific physical properties to aid in the separation. The column is coiled inside a thermostatted oven. Oven temperature is an important variable in the separation and must be controlled to a few tenths of a degree. The mobile phase is usually an inert gas such as He. The continual flow of the carrier gas through the column is controlled by a two-stage pressure regulator at the gas cylinder and a flow controller. The pressure at the inlet of the column is greater than the pressure of the outlet of the column. This pressure differential helps force the mobile phase through the column. The flow of carrier gas through the column is assumed to be constant if the pressure differential across the column does not change.

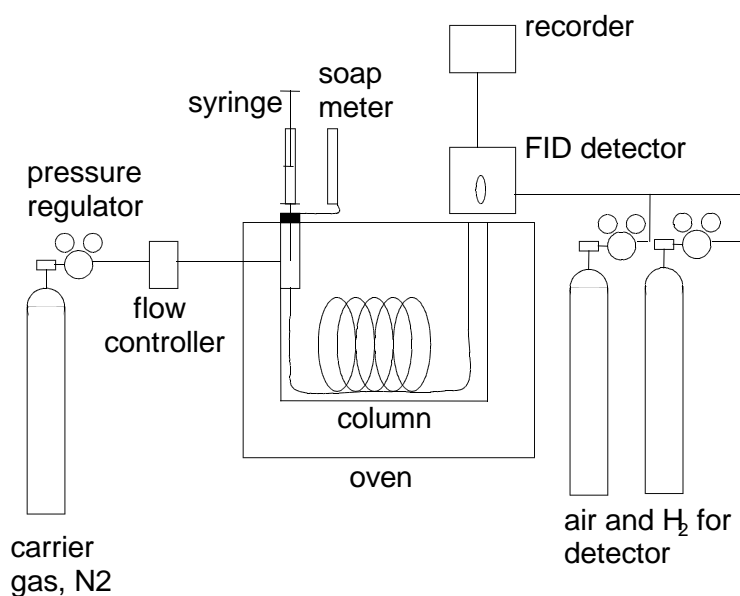


Figure 1: Diagram of gas-liquid chromatograph.

The sample eventually leaves the column and passes into the detector, which responds to any change in the chemical or physical nature of the gas leaving the column. There are several types of detectors that can be coupled to the column. In this experiment a flame ionization detector (FID) is used. The effluent from the column is passed through a hydrogen/air flame. Most organics, when pyrolyzed at this temperature, will produce ions and electrons that can be conducted electrically through the flame. A potential difference is applied across the burner tip and a collector electrode above the flame. The resulting current is measured. The magnitude of the output depends on the partial pressure of the solute in the gas and the sensitivity of the detector to the sample. The output is recorded as amount of solute leaving the column as a function of time; this is the chromatograph, shown in Figure 2.

The flow rate of carrier gas is measured outside the column, usually at the outlet where the temperature and pressure are those of the surroundings. The flow rates of the carrier gas can be measured by a flow meter. In this experiment a soap-bubble flow meter is used. Soapy water is contained in a rubber bulb attached to the end of a calibrated glass volume. When the rubber bulb is squeezed a soapy film is formed in the path of the carrier gas. The soapy film travels with the carrier gas; the time required for the film to travel between two markers on the calibrated volume is measured and converted into a volumetric flow rate. In order to calculate a flow rate which corresponds to the actual column conditions two corrections must be applied to the measured flow

rate. The first correction takes into account the fact that the flow rate is measured at room temperature and pressure. When the carrier gas enters the flow meter, it becomes mixed with water vapor; hence the partial pressure of the gas in the flow meter is less than the barometric pressure, P . It is assumed that the carrier gas is saturated with water vapor, therefore the partial pressure of the gas in the flow meter is $P - P_w$, where P_w is the vapor pressure of water at the temperature, T , of the flow meter. The flow rate at pressure and temperature, T_c , of the column is obtained from the measured flow rate, F_m , by applying the ideal gas law:

$$F = F_m \cdot \frac{T_c}{T} \cdot \frac{P - P_w}{P} \quad (1)$$

The second correction takes into account the fact that there is a pressure drop across the column. The average column pressure is $\frac{1}{2}(P_{\text{inlet}} + P_{\text{outlet}})$. According to Boyle's law the average flow rate, F_{ave} , is related to F by

$$F_{\text{ave}} = F \cdot \frac{P}{P_{\text{ave}}} \quad (2)$$

The ratio of P to P_{ave} is known as the compressibility factor, j . (This compressibility factor is not the same as the compressibility factor, z , for an ideal gas.)

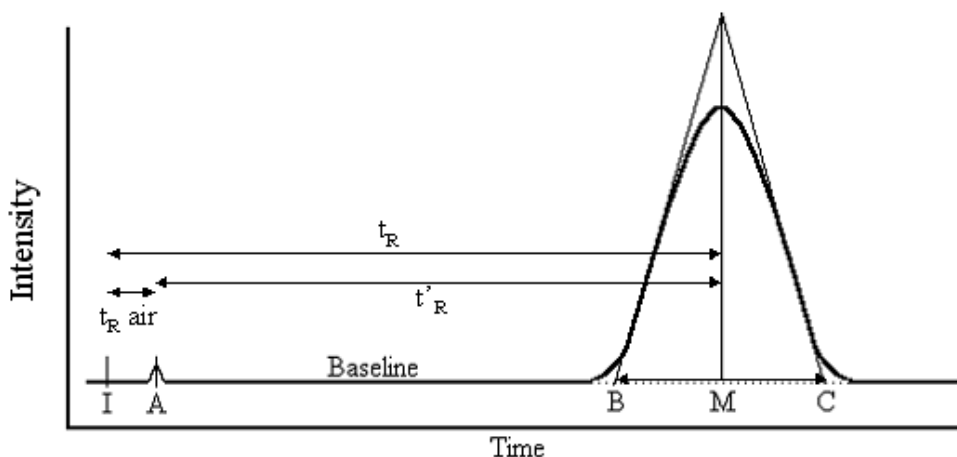


Fig. 2: Idealized Elution Diagram, where I = injection point, A = air peak, M = solute peak, BC = base width of peak, $t_{R \text{ air}}$ is the retention time of the air peak, t_R is the retention time of the solute and t'_R is the corrected retention time of the solute.

Under the proper conditions a sample typically moves along the column in a gradually broadening band. The middle of the band corresponds to the maximum concentration, thus the output will resemble a Gaussian shaped peak. Because the flow rate of the carrier gas is well-defined the distance between the peak maxima (M) and the

point of injection of the sample (I) corresponds to the time during which half of the sample was held on the column. This time is known as the "retention time", t_R , of the solute, and is a characteristic of the solute for a given stationary phase, column temperature, and carrier-gas flow-rate. This quantity is found directly from the chromatograph. It is necessary to make a correction which takes into account the time to elute the carrier gas that is already on the column when the sample is injected. This correction can be obtained by measuring the retention time for a solute that does not interact with the mobile phase. In practice this correction can be easily found because when the sample is injected into the instrument some air is also injected. The air is not absorbed by the solvent to any appreciable extent and passes through the column with the carrier gas. The detector records the "air peak" (A) and the time between the appearance of the air peak and the solute peak, is the corrected retention time, t'_R . However, in this particular instrument, the FID detector does not produce an air peak. Instead, the time required to elute the air peak is found from a calibration curve which relates the flow rate of carrier gas to the air peak retention time. This curve has been previously measured for this particular instrument and is given in Appendix 1.

By multiplying the corrected retention time by the average carrier gas flow rate, one removes the dependence on carrier gas flow rate and gains a more significant quantity, the "net retention volume" of the solute. The net retention volume, V_N , is the volume of carrier gas needed to elute one-half of the solute from the column.

$$V_N = j F t'_R \quad (3)$$

The value of V_N , calculated by eq. 3, is a function of not only the solvent and solute used, but also the column temperature and the amount of solvent on the column. In order to eliminate the dependence on the two latter quantities and obtain a retention volume which is uniquely characteristic of the solute-solvent system, a "specific retention volume", V_g , is often reported. The specific retention volume is the volume of carrier gas, corrected to 273 K, which will elute one-half of the solute per gram of solvent in the column. Thus,

$$V_g = \frac{V_N}{G} \cdot \frac{273}{T_c} \quad (4)$$

where G is the weight of solvent on the column. In this particular experimental setup, the total load on the column, the stationary phase and the solid support, is 12.79 ± 0.01 g. The stationary phase is dinonylphthalate, which is 16.0 ± 0.1 % of the total weight.

Many uses of GLC involve the separation of a mixture of components. If an appropriate mobile phase has been chosen, the components in a mixture will vary in the

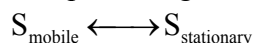
extent to which they distribute themselves between the two phases. The components will move through the column at different rates and will enter the detector at different times, thus not one but several peaks will be recorded with different retention times and volumes. If the column is long enough, the components will be completely separated and can be identified if the retention times of the individual components have been established. Furthermore, the relative areas under the separate peaks provide a means of estimating the relative amounts of the various components. The degree of separation can be controlled by changing the oven temperature, mobile phase, stationary phase or column length. The resolution between two peaks is given by the ratio of the distance between two peak maxima to the mean value of the peak width.

$$\text{Res} = \frac{2((t_r)_a - (t_r)_b)}{(w_a + w_b)} \quad (5)$$

Here $(t_r)_a$ and $(t_r)_b$ are the retention times and w_a and w_b are the widths at the baseline of peaks a and b, respectively. The value of w is estimated by drawing the best isosceles triangle through the peak and measuring the width at the base line. Baseline resolution is achieved when $\text{Res} = 1.5$.

So far we have dealt with parameters which are readily obtained from experimental data without considering the theory which relates retention volumes to physical properties that influence separation. In 1941 Martin and Synge pioneered a theory which explains the migration and separation of the solute on a GLC column. Plate theory successfully accounts for the rate of movement down a column and the Gaussian shape of the peaks in the chromatograph. However in plate theory, effects such as diffusion and the finite rate of mass transfer of the solute on the column are ignored. Later, rate theory was developed as a modification to plate theory to incorporate these effects. In spite of the shortcomings of plate theory, it is an effective model when applied to the proper situations and is more useful for the purposes of this experiment. One can therefore have reasonable confidence in the relationships obtainable from plate theory.

Plate theory treats the column as if it were divided into N "theoretical plates." Each theoretical plate is assumed to contain the same volume of carrier gas and the same volume and weight of solvent. In each plate, equilibrium is assumed to exist in the distribution of the solute between the liquid and gaseous phases.



This equilibrium condition can be expressed as:

$$C_s / C_m = K \quad (6)$$

where K is the equilibrium constant, termed the partition coefficient, C_m and C_s are the molar concentrations of solute in mobile and stationary phases, respectively. The partition coefficient depends only on the temperature for a given solute-solvent pair, provided that the concentrations are low enough so that the solute can be considered to behave ideally in the gaseous phase and to obey the laws of dilute solutions in the liquid phase. The analyte moves down the column in a series of distinct steps in which a new equilibrium is established. A theoretical plate can therefore be defined as the distance required for complete equilibrium to be established between the two phases.

The partition coefficient can be calculated from the net retention volume

$$V_N = KV_S \quad (7)$$

Where V_S is the total volume of stationary phase, or solvent, in the column. Equation 7 is an important equation in plate theory because it relates an experimental quantity, V_N , to a thermodynamic quantity, K . Since V_S is constant for a given column, equation 7 presents a partial explanation of the ability of GLC to separate the components of a mixture.

The number of theoretical plates in the column, N , is calculated from:

$$N = (4d/w)^2 \quad (8)$$

where d is the distance of the elution peak from the injection point, as measured on the recorder (IM in Fig. 2), and w is the width of the peak at its base (BC in Fig. 2). It is possible to calculate the theoretical plate height (HETP), given that

$$\text{HETP} = L/N \quad (9)$$

where L is the length of the column. The plate height is proportional to the width of a band and the distance that it has traveled. The column efficiency can be described by the number of theoretical plates. The separation of a mixture improves and the peaks become narrower as the number of theoretical plates increases. The resolution is proportional to the square root of the number of plates in the column.

In a GLC, the components of a mixture are separated due to their difference in solubilities in the stationary phase. Therefore, each component must have a different partition coefficient. From the partition coefficient the activity coefficient of the solute can be found. The activity coefficient, γ , is a unitless quantity that can be multiplied by the true concentration of a species to find an effective concentration. The effective concentration is often used when the true concentration does not give a good indication of the chemical effectiveness of a species. In other words, [the activity coefficient is a measure of the effectiveness with which the species of the solute influence an equilibrium which it is a participant in](#). The activity coefficient gives an indication of departure from ideal conditions. For ideal gases and dilute solutions the activity coefficient is unity and

the effectiveness of each molecule is equal to its theoretical effectiveness. In the following discussion it is assumed that the amount of solute injected onto the column is small enough so that the ideal gas and dilute solution laws are obeyed in every plate of the column. The activity of the solute, a , in the stationary phase of each solute-containing plate is given by Henry's law:

$$a = \gamma X_1 \quad (10)$$

where the standard state of the solute is the pure liquid, γ is the activity coefficient of the solute, and X_1 is the mole fraction of solute in the liquid phase (the stationary phase).

It is possible to use equation 7, which relates an experimentally measurable parameter, V_N , to the partition coefficient to solve for the activity coefficient. The first step is to find the concentrations of the solute in the mobile and stationary phase in terms of experimental quantities. If we assume that the solute vapor behaves ideally it is possible to solve for the concentration of the solute in the vapor phase.

$$C_m = \frac{P^0 \gamma X_1}{RT_c} = \frac{P^0 \gamma n_1 M_s}{RT_c g_s} \quad (11)$$

Here P^0 is the vapor pressure of the pure liquid solute, R is the ideal gas constant, T_c is the temperature of the oven, n_1 is the number of moles of solute in the stationary phase in a plate, M_s is the molecular weight of the solvent and g_s is the grams of solvent in each plate. The concentration of solute in the stationary phase can be written as the ratio of moles of solute in the stationary phase in a plate, n_1 , to the volume of the stationary phase in each plate, v_s .

$$C_s = n_1 / v_s \quad (12)$$

The partition coefficient can now be written as

$$K = \frac{RT_c g_s}{P^0 \gamma M_1 v_s} = \frac{RT_c G}{P^0 \gamma M_1 V_s} \quad (13)$$

In equation 12, $g_s/v_s = G/V_s$, both are the density of the solvent. This representation of K can now be substituted into equation 7.

$$V_N = \frac{RT_c G}{P^0 \gamma M_1} \quad (14)$$

This equation relates the experimental value, V_N , to the activity coefficient, γ . It is more appropriate to solve for the activity coefficient in terms of the specific retention volume, V_g , instead of the net retention volume, V_N . In doing this, one removes the dependence on such column parameters as T_c and G , though P^0 is a very sensitive function of the temperature. Solving for the activity coefficient in terms of V_g gives:

$$\gamma = \frac{273 \cdot R}{V_g P^{\circ} M_1} \quad (15)$$

To restate, M_1 is the molecular weight of the stationary phase, R is the ideal gas constant, and P° is the vapor pressure of pure liquid solute, which can be found from the Antoine equation. The effectiveness of a column in separating several different solutes can be assessed by comparing V_g values. Thus, while P° is usually the main factor in determining separability, one must not overlook the possibility that the different solutes may have widely differing degrees of non-ideality and hence different γ values in a certain solvent.

Experiment

DO NOT CHANGE ANY SETTING ON THE INSTRUMENT except as indicated below. They have been preset to give proper operating conditions. A picture of the instrument is shown in Appendix 2.

Record the column data — total load (weight) and percent loading of solvent in the column (posted on card on instrument.) Solvent: dinonyl phthalate (molecular weight = 419); solid support: Chromosorb P, 60-80 mesh, acid washed (a commercial product made from diatomaceous earth and clay).

The GC uses a flame ionization detector in which a hydrogen flame is used to ionize the effluent of the column. Consequently the flame must be off in order to measure the flow rate of the carrier gas. Also the flame ionization detector will NOT detect the "air peak" shown in Fig. 2. The time of the appearance of the "air peak" after injection is determined from a graph by the instrument using the measured flow rate.

The instrument should be warmed up for one hour.

The flow rate of the carrier gas is set. DO NOT CHANGE IT. To measure the flow rate raise the detector cover and make sure that the toggle valves at the back of the detector are closed (down position). Place the end of the tube connected to the bubble flow meter firmly over the outlet of detector "A." Start a bubble using the bulb at the bottom of the flow meter and, using a stopwatch, time the bubble from the 1 to the 10 mL mark. Do this several times and take an average. Remove the tube from the detector outlet.

Record the inlet and outlet pressures of the column. There is a mercury manometer attached to the instrument. One side is connected to the inlet of injector A and the other side open to the atmosphere. The outlet of the column is open to the atmosphere so that the outlet pressure is atmospheric pressure. The manometer measures

the inlet pressure relative to atmospheric pressure. The column temperature is set to 65 Celsius and controlled to a tenth of a degree.

Starting the flame detector: Open the two toggle valves for detector "A" and set the regulator on the air tank to 8 psi. Set the regulator on the hydrogen tank to 20 psi. Use the glow plug on the top of the detector to ignite the flame. Place a small beaker over the detector and inspect for water condensing on the bottom (the hydrogen flame is invisible). This indicates that the flame is lit. Slowly increase the air pressure to 22 psi. Recheck with the beaker.

Five injections are made: One injection each of benzene, cyclohexane, cyclohexene, and two injections of an equal volume mixture of the three. Use 1 μL of the individual compounds and 3 μL of the mixture. Handle the microliter syringe carefully. The needle especially is fragile. Draw approximately 1 μL of air into the syringe then the sample then more air until you can see the liquid in the glass barrel of the syringe. Insert the full length of the needle carefully into the injection port. Now simultaneously inject the sample, and press the start button on the chart recorder. Retention times are between 8 and 16 minutes for a column temperature of 65 Celsius and a flow rate of 40 mL/min. Do not inject the next sample until the peak has been plotted on the chart recorder and the pen returned to the baseline.

When all injections are finished, close the toggle valves on the detector and measure the inlet and outlet column pressure again. If the pressure has changed, remeasure the flow rate and use the average.

Before leaving the lab one should have recorded:

- the barometric pressure and room temperature, before and after the experiment.
- the pressure differential across the column before and after the experiment
- the oven temperature
- the air retention time for a given carrier gas flow rate
- record the type of stationary phase used as well as the weight of stationary phase on the column

Calculations and Discussion

1. Calculate the corrected flow rate, F .
2. Identify the peaks in your chromatogram of the mixture. Calculate the resolution of adjacent peaks on the chromatogram.
3. For each of the pure liquids used calculate:
 - a. the adjusted retention time, t'_R .

- b. the net retention volume V_N .
 - c. the specific retention volume, V_g .
 - d. the value of P° at T_C for each of the solutes studied (see * below)
 - e. the activity coefficient, γ
 - f. the number of theoretical plates, N , in the column.
 - g. Give your values of HETP for the column (in cm) for each of the liquids.
Assume that the column is 4 ft long.
4. Estimate the uncertainty in each experimental value (#1 and 3 a-g) calculated above.

* note (part 3d) The vapor pressure of many liquids can be fitted very closely, for temperatures between the triple point and well above the normal boiling point, by the Antoine equation

$$\log(P) = A - \frac{B}{t + C}$$

where P is the vapor pressure in mm of Hg and t is the centigrade temperature.

For the liquids studied, the constants A , B , and C are:

	A	B	C
benzene	6.90565	1211.033	220.790
cyclohexane	6.84498	1203.526	222.863
cyclohexene	6.88617	1229.973	224.104
2-butanone	6.38469	916.01	181.84

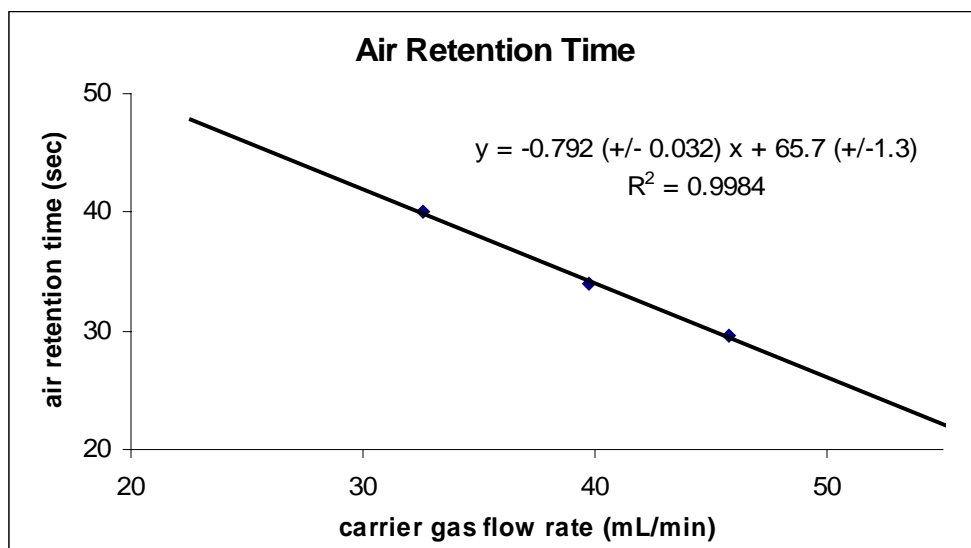
Include in your discussion:

- A comparison of your γ values for benzene, cyclohexane, and cyclohexene with the values found in the literature, (see ref. 6)
- An explanation of the differences in the γ values found. Do the γ values make sense when compared to the retention times?
- The ratio of P to P_{ave} is the compressibility factor, j . Equation 2 assumes that the pressure drop across the column is linear. When the ratio of P_{inlet}/P_{outlet} is less than 1.5, little error is made in this assumption, however in this experiment P_{inlet}/P_{outlet} is slightly larger than 1.5. How does this affect your results? For a more accurate estimation of j , one would use $j = (3/2)[(R^2 - 1)/(R^3 - 1)]$, where $R = P_{inlet}/P_{outlet}$.
- A discussion of the factors which cause positive and negative deviations from ideal solution behavior.

- A discussion of the factors which enter into the selection of a solvent and the column conditions used when various types of organic substances are being separated by GLC.

References:

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Appendix 1: Air Retention Time

Appendix 2: Picture of the instrument

