

PHASE EQUILIBRIA STUDIES WITH BROMINE

A THESIS

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PHASE EQUILIBRIA STUDIES WITH BROMINE

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ABSTRACT

PHASE EQUILIBRIA STUDIES WITH BROMINE

A study of the liquid-vapor equilibria of three binary systems, each consisting of bromine and an organic solvent was made. The experimentally obtained results were compared with predictions based on the properties of the components, and on the interaction between the components of each system as measured by volume change on mixing. This investigation is a continuation of work by Spicer and Kruger, and by Spicer and Meyer. The work was initiated to discover binary azeotropes consisting of one colored and one colorless component. Azeotropes of this type are valuable in the study of methods for separating azeotropic mixtures, for the extent of separation can be ascertained merely by visual observation.

The equilibrium still used in this investigation was modified from a similar still described by Jones, Schoenborn, and Colburn. A scale drawing of the modified still is presented. All equilibria were studied at 760 mm pressure.

The System Bromine-Trichloromonofluoromethane.--In this system, the boiling point increases regularly as the mole fraction of bromine in the liquid is increased. No azeotrope is formed.

The System Bromine- 1,1-dichloro-2,2-difluoroethane.--In this system an azeotrope is formed with a composition of 0.581 mole fraction

bromine, and a boiling point of 49.6° C. The per cent increase in volume on mixing bromine with the solvent of this system was found to be about 1.8, and noticeable cooling occurred. This indicates that the deviation from Raoult's law is greater in this system than in the system following, but this conclusion is inconsistent with the estimated internal pressures. This inconsistency can be explained by the probability of greater hydrogen bonding between the molecules of this solvent, than between the molecules of the solvent of the system following.

The System Bromine- 1,2,2-trichloro-1,1-difluoroethane.--In this system an azeotrope is formed with a composition of 0.747 mole fraction bromine, and a boiling point of 54.6° C. The per cent increase in volume on mixing bromine with the solvent of this system was found to be about 0.3. Slight, but noticeable cooling occurred on mixing.

Measurements of the refractive indices of the solvents of the second and third systems before and after contact with bromine, support the contention that no reaction takes place between these solvents and bromine. The smoothness of the equilibrium curves is further evidence that no reaction takes place between the solvent and bromine in any of the systems investigated.

Comparison of the system bromine-trichloromonofluoromethane and the system bromine- 1,2,2-trichloro-1,1-difluoroethane with the system bromine-benzotrifluoride, indicates that benzotrifluoride must be associated to a greater extent than are trichloromonofluoromethane or 1,2,2-trichloro-1,1-difluoroethane.

CHAPTER I

INTRODUCTION

PHASE EQUILIBRIA STUDIES WITH BROMINE

CHAPTER I

INTRODUCTION

In the development of methods for separating azeotropic mixtures, it is convenient to work with constant boiling mixtures containing one colored component, for separation of the colored component can be determined by direct visual observation. Because of its intense color, bromine was suggested as a suitable component for such mixtures. Spicer and Kruger¹ investigated the system bromine-carbon tetrachloride and proved the existence of an azeotrope in this system. Spicer and Meyer² found azeotropes in other systems in which bromine was a component. This investigation is a continuation of the work done by Spicer, Kruger and Meyer.

Because of the high reactivity of bromine, and the fact that azeotrope formation is not likely to occur when the difference between boiling points of the components is large,³ the choice of inert bromine solvents was difficult. It was also desired that such solvents

¹W. M. Spicer and J. Kruger, J. Am. Chem. Soc., 72, 1855 (1950)

²W. M. Spicer and L. H. Meyer, J. Am. Chem. Soc., 73, 934 (1951)

³R. H. Ewell, J. M. Harrison, and L. Berg, Ind. Eng. Chem., 36, 871 (1944)

should be completely miscible with bromine. The search was begun with completely halogenated, saturated hydrocarbons. Only trichloromono-fluoromethane met the above requirements, had not been previously investigated, and was also available in quantity. The low boiling point of this compound made azeotrope formation, except at low bromine concentrations, very unlikely. Because this compound was readily available, however, it was used for an initial study.

In general, compounds containing a halogen atom on each carbon atom will not readily undergo substitution reactions with bromine. It has been observed also, that compounds in which two fluorine atoms are attached to the same carbon, are considerably increased in stability.^{4,5} In view of this, it was decided that partially halogenated compounds containing the CF_2 group would probably be inert to bromine in the absence of a catalyst. Vapor-liquid studies were therefore made on systems consisting of bromine and 1,1-dichloro-2,2-difluoroethane, and of bromine and 1,2,2-trichloro-1,1-difluoroethane.

A detailed report on the investigation of the vapor-liquid equilibria of these three systems follows in the ensuing chapters.

⁴A. L. Henne and Thomas Midgley, Jr., J. Am. Chem. Soc., 58, 882 (1936).

⁵J. H. Simons, Ind. Eng. Chem., 39, 240 (1947).

CHAPTER II

APPARATUS AND MATERIALS

CHAPTER II

APPARATUS AND MATERIALS

Apparatus

Equilibrium Still

All liquid-vapor equilibria data was obtained from an equilibrium still, a scale drawing of which is shown in Figure 9. Originally this still was made according to the specifications of a similar still whose design and operation is described by Jones, Schoenborn, and Colburn.⁶ Additions and modifications were made by Kruger and by Meyer. The still was rebuilt for this investigation, and further slight modifications were made.

As can be seen from Figure 9, the equilibrium still is constructed entirely of glass. The flash boiler, residue chamber, and vapor line each has a separate coil of nichrome wire, connected through a General Radio Company Variac to a Sola constant voltage transformer. The adjustment of the voltage applied to the residue chamber coil must be carefully controlled, and is dependent on the voltage applied to the flash boiler. For this reason, after the first system had been studied, a voltmeter having a zero to ten volts scale was placed in parallel with the residue chamber coil. Both the residue chamber and

⁶C. A. Jones, E. M. Schoenborn, and A. P. Colburn, Ind. Eng. Chem., 35, 666 (1943)

flash boiler coil Variacs were connected through one Superior Electric Co. Powerstat to the Sola constant voltage transformer. With this arrangement, large fluctuations in line voltage, not smoothed out by the constant voltage transformer, could be quickly compensated for by adjusting the Powerstat until the voltmeter returned to a reading previously determined as being correct.

The residue chamber and vapor line were covered with insulation formed from asbestos paste, except for a small window on the residue chamber, provided so that the liquid level could be observed.

A large glass tank, not shown in Figure 9, was kept full of crushed ice. Cold water from the melting ice was pumped through the two condensers, allowed to trickle over the crushed ice, and recirculated. In studying the first system, it was necessary to place a cooling coil of glass around the lower portion of the residue chamber, and to pump ice water through this also. This was because the boiling point of the solvent, trichloromonofluoromethane, was sometimes below room temperature. Without the cooling coil, vapor bubbled through the residue chamber too fast to reach equilibrium with the liquid phase there, and caused such an overload on the flashboiler that entrainment resulted.

As the weather became warm and humid, water condensing from the air on the cold outer surfaces of the condensers presented a problem. This water dripping on the flashboiler completely upset operation of the instrument, and in dripping down the distillate chamber delivery tube, threatened to contaminate samples. Devices were made of paper

insulated wire, and of glass wool, that effectively controlled this water so that it dripped harmlessly onto sponges provided for this purpose. These devices are not shown in Figure 9.

To minimize the loss of bromine vapor into the atmosphere, the two delivery tubes were equipped with standard taper ground glass joints. Erlenmeyer flasks were equipped with corresponding female ground glass joints, and were used to introduce liquid into the equilibrium still.

A cold trap, shown in Figure 9, was surrounded by a thermos bottle full of dry ice throughout all runs. This trap prevented moisture from entering the system, and also prevented the highly corrosive bromine vapor from entering the pressure tank.

As indicated in Figure 9, a two-way stop-cock opened the equilibrium still to a water aspirator, or to a pressure tank. This large leak-proof metal tank was equipped with a 1/6 HP compressor, and was connected to the glass tube leading from the equilibrium still by heavy rubber tubing. The tank and compressor were used to maintain the pressure in the equilibrium still at 760 mm. A mercury manometer, connected to the glass tube leading to the pressure tank, was used for reading gage pressure.

A copper-constantan thermocouple, inserted into a thermocouple well in the residue chamber, was used to measure equilibrium temperatures. The cold junction was in a bath of finely crushed melting ice, held in a dewar flask surrounded by asbestos insulation. The thermocouple was connected to a Leeds and Northrup No. 7651 potentiometer reading to 0.001 millivolt. This number of millivolts corresponds to

about 0.01 degrees centigrade. Variations in the potentiometer circuit and fluctuations in the operation of the still, made the recorded equilibrium temperatures accurate to only about 0.1° C. In rebuilding the apparatus for this investigation, it was necessary to make a new copper-constantan thermocouple. The thermocouple was calibrated against a corrected 100° x 0.1° C, 76 mm immersion thermometer.

A device for removing all traces of water from the equilibrium still is indicated in Figure 10. By means of the water aspirator, air was bubbled through concentrated sulfuric acid, was passed over soda-lime, and then into the equilibrium still. When necessary, the still was also warmed by means of the three heating coils already discussed.

The Large Fractionating Column

A five foot glass helix packed column was used to purify 1,1-dichloro-2,2-difluoroethane and 1,2,2-trichloro-1,1-difluoroethane. This column was also used to separate pure solvent from a mixture of bromine and solvent, in testing for the possibility of reaction.

The column was equipped with a heating coil of nichrome wire, connected through a General Radio Company Variac to a Sola constant voltage transformer. The distilling flask was heated by means of a Glas-Col heating mantle, connected in the same way. An air gap insulated the column from the surrounding atmosphere.

During all runs, a reflux ratio of more than 20-1 was maintained, and ice water was circulated through the condenser.

The Small Fractionating Column

This column has a packed section about 40 centimeters long and

2 centimeters in diameter, and is packed with 3/16 inch glass helices. The column is insulated with glass wool. Heat was applied by a Glas-Col heating mantle which surrounded the distilling flask. The column is equipped with standard taper ground glass joints for distilling flask, thermometer, and take-off. A glass tube led from the condenser to a cold trap which was surrounded by dry ice during all runs. During operation, a rubber tube led from the cold trap mentioned above, to the distillate chamber delivery tube of the equilibrium still. In this manner the pressure control apparatus described above, could be used to maintain a pressure of 760 mm on the column. As will be explained later, this column was used to prepare azeotropes.

Apparatus for Measuring Volume Change on Mixing

The apparatus for measuring volume change on mixing consisted simply of two ten milliliter burets, and a small graduated cylinder. The graduated cylinder was made by sealing and rounding the tip of a ten milliliter pipet. The pipet was cut at the four milliliter mark, and a ring of glass beads was attached just below this mark so that the cylinder could be hung.

The cylinder was calibrated for reading the top meniscus, by measuring a number of samples of potassium permanganate solution in water, into the clean dry cylinder from each of the burets.

Materials

Bromine

Baker's analyzed C. P. bromine was used for all systems. No further purification was performed.

Solvents

Trichloromonofluoromethane.--This solvent, "Freon 11," was contributed by the "Kinetic" Chemicals Division of E. I. du Pont de Nemours & Co.. Except for straight distillation in all glass apparatus, no further purification was performed.

1,1-dichloro-2,2-difluoroethane.--This compound was purchased from Halogen Chemicals Inc., and was stated by its manufacturer to be better than 95 per cent pure. Further purification was performed by fractional distillation in the larger column described above. An account of this distillation will be found in Table 2, and in Figure 3. A middle cut consisting of fractions four through eight was used.

1,2,2-trichloro-1,1-difluoroethane.--This compound was also purchased from Halogen Chemicals Inc., and was stated by its manufacturer to be better than 95 per cent pure. Further purification was performed by fractional distillation in the larger column. Data on this distillation will be found in Table 4, and in Figure 6. A middle cut consisting of fractions four through nine was used.

CHAPTER III

PROCEDURE AND RESULTS

CHAPTER III

PROCEDURE AND RESULTS

General Procedure for Operating the Equilibrium Still

Before studying each system the equilibrium still was thoroughly cleaned, rinsed several times with distilled water, rinsed with acetone, then dried by drawing air from the drying train of Figure 10 through the apparatus over night.

Pure solvent was then introduced into the apparatus. With ice water circulating through the condensers, and only the flash boiler heater on, an Erlenmeyer flask fitted with a standard taper female ground glass joint and containing at least 25 ml of solvent, was loosely attached to the distillate chamber delivery tube. The delivery tube stopcocks were closed and the aspirator was adjusted so that the pressure within the apparatus was only slightly less than that of the atmosphere. The distillate chamber stopcock was slowly opened so that liquid was drawn into the distillate chamber, and overflowed through the flash boiler into the residue chamber. The delivery tube reached almost to the bottom of the Erlenmeyer flask, so that very nearly all of the contents could be introduced into the apparatus.

The two-way stopcock was then opened to the pressure tank which had been opened to the atmosphere. Barometric pressure was determined, and enough gage pressure was applied to the tank to correct the pressure within the equilibrium still to 760 mm. Both barometric and gage

pressures were checked several times during each run, and the gage pressure of the tank changed if necessary.

Once the still had been filled, and the pressure adjusted, it was necessary to regulate the heat supplied to the flash boiler, residue chamber, and vapor line. The regulation of heat supplied to the vapor line was not sensitive, for it was only required that the temperature of the vapor line be greater than that of the residue chamber. This precaution prevented vapor from condensing back into the liquid phase, and prevented refluxing and therefore fractionation. The flash boiler temperature was adjusted so that a steady stream of vapor bubbled around the thermocouple well. If this stream of bubbles was not sufficiently great, the liquid in the residue chamber was not maintained at equilibrium temperature, and the temperature read was very sensitive to very slight changes in the adjustment of the residue chamber heating coil. On the other hand, if too much heat was supplied to the flash boiler, vapor bubbled through the residue chamber too rapidly to attain equilibrium.

The most sensitive adjustment was that of the heat supplied to the residue chamber. If insufficient heat was supplied, vapor leaving the flash boiler would condense in the residue chamber and operation would cease. If too much heat was supplied, the flash boiler would be overloaded and liquid collecting there would be entrained with vapor into the residue chamber. This adjustment was dependent on the heat supplied to the flash boiler, for a rapid stream of vapor passing through the residue chamber brought in more heat energy than did a slow stream. To a lesser, but noticeable extent, this adjustment was also dependent

on the rate of circulation of condenser cooling water. The heat supplied to the residue chamber was so adjusted that liquid was at all times maintained at the bottom of the flash boiler, so that superheating in the flash boiler could not occur. This heat was also so adjusted that this liquid at the bottom of the flash boiler did not increase in volume enough to be entrained into the residue chamber. When all these conditions had been fulfilled, it was felt that the temperature read was the true equilibrium temperature. It was observed experimentally, that if liquid did not quite reach the bottom of the flash boiler the temperature reading was low, and that if a pool of liquid collected at the bottom of the flash boiler the temperature reading was high.

When these conditions had been maintained sufficiently long for equilibrium to be reached, the temperature was determined by means of the thermocouple and potentiometer already described. Several readings were taken over a period of at least half an hour to be sure that equilibrium had been reached.

After thus obtaining the boiling point of pure solvent, runs were made with solutions of the solvent and bromine ranging from 0 per cent to 100 per cent bromine. Between each of these runs, the equilibrium still was dried by passing air from the drying train of Figure 10 through the still over night. The procedure of introducing solutions and determining their equilibrium temperatures was identical to that given above for pure solvent. Since vapor and liquid phases differed greatly in composition for each of these solutions, however, about an hour was allowed for equilibrium to be reached. The procedure followed in analyzing the liquid and vapor phases of these solutions will be presented

below.

General Method of Analysis

Because of the volatility of the liquids, they were weighed in ground-glass stoppered weighing bottles. A number of weighing bottles of approximately 50 ml capacity and about 45 grams in weight were used. The two bottles having the least weight were marked and each was used as a counterpoise. In preparation for each run, 20 ml of a solution of potassium iodide, so made up that each 20 ml contained 3.072 grams of potassium iodide, was poured into each of eight of these bottles. The bottles were placed in a shallow, hard rubber pan, and crushed ice was packed around them so that the ice did not extend much above the liquid level inside of the bottles.

From the material already presented, it has probably been gathered that the liquid in the distillate chamber is condensed vapor phase, and that vapor of this composition is in equilibrium with the liquid phase which is in the residue chamber. The small amount of liquid in each chamber which might have remained stagnant during the run was withdrawn. The residue chamber and vapor line heating coils were immediately cut off to prevent further evaporation of the liquid phase. The flash boiler heating coil was left on to prevent liquid from being drawn into the flash boiler from the residue chamber.

One of the prepared bottles marked for use as a counterpoise, and a second bottle was removed from the crushed ice mentioned above. The bottles were checked to insure that no moisture was present on the ground glass of their necks, dipped in acetone to remove traces of water, dried

with clean paper towels and weighed. The counterpoise was placed on the right hand balance during weighing, and recording of the last two significant figures was delayed until the cold weighing bottles reached a stable weight. Beakers of dry silica gel placed in the balance case seemed to make the amount of moisture condensing on the bottles slightly less.

A few drops of liquid from the distillate chamber delivery tube were then quickly introduced into the second weighing bottle, holding the tip of the delivery tube close to the surface of the potassium iodide solution. This bottle was then quickly reweighed, using the counterpoise as before. Care was taken to handle the weighing bottle and counterpoise in just the same way. The liberated iodine was titrated with approximately 0.2 N standardized sodium thiosulfate solution to a starch indicator end point.

The counterpoise just used was returned to the pan of crushed ice for later use. A second counterpoise and another of the prepared weighing bottles was used to analyze the contents of the residue chamber, following the procedure outlined above. This procedure was followed until three samples had been analyzed from each of the chambers. Agreement was generally quite good, and the average analysis of the samples was taken as the concentration of each phase.

The sodium thiosulfate solutions were stabilized by the addition of 0.1 gram sodium carbonate per liter of solution.⁷ These solutions were standardized by titration against 0.2000 N potassium dichromate solution,

⁷Rieman, Neuss, and Naiman, Quantitative Analysis, Second edition, (New York and London: McGraw-Hill Book Company Inc., 1942), p. 221.

prepared by direct weighing.⁸ Starch solutions contained mercuric iodide as a preservative, and were made up by the directions of Kolthoff and Sandell, except that potato starch was used.⁹ The procedure used in standardizing sodium thiosulfate solutions against potassium dichromate solution was adapted from the procedure given in Kolthoff and Sandell.¹⁰ Practically no change occurred in the standard of the sodium thiosulfate solutions in the time required for their consumption, as verified by frequent checks.

The System Bromine-Trichloromonofluoromethane

Operation of the Equilibrium Still.—Because of the low boiling point of this system a number of difficulties were encountered. As has been explained previously, it was necessary to construct a cooling coil for the residue chamber, in order that the heat applied to this portion of the still could be controlled. It was also desirable that the condensed vapor in the distillate chamber be kept well below its boiling point. Much of the work on this system was done in cold weather, and the laboratory windows were opened to keep the room temperature low.

In introducing solvent-rich solutions into the still, care had to be taken to prevent the liquid from suddenly boiling and entraining liquid into the cold trap. Only cold solutions were so introduced, and care was taken to decrease the pressure within the still only enough to cause liquid to be drawn in.

⁸Kolthoff and Sandell, Textbook of Quantitative Analysis, (New York: The MacMillan Co., 1947), p. 608.

⁹Ibid., p. 619.

¹⁰Ibid., p. 624.

A thin film of Dow-Corning silicone stopcock grease was used on the stopcocks in studying this system.

Method of Analysis.--The general method of analysis already presented was evolved to deal with the high volatility of this solvent. At first, the weighing bottles of potassium iodide solution were cooled in dry ice until crystals began to form. This proved to be impractical, however, for moisture condensation on the surface of the weighing bottles was so great as to make weighings less exact. Also, the crystals so formed had to be melted before titration could be completed. The method followed is identical to that already presented, except that the weighing bottles were kept somewhat colder than they were when the other systems were studied. It was especially true in studying this system that the bottles had to be weighed quickly after introducing samples into them. As a further precaution, the bottles were again plunged into ice after being weighed, and were kept there until the samples could be titrated less than a minute later. Agreement between several analyses were usually fairly good to the third decimal, as expressed in mole fractions.

Results from Fractionating Column.--Data obtained from the equilibrium still indicates that no azeotrope is formed in this system. As a final assurance that no azeotrope is formed at 760 mm pressure near the solvent-rich end of this system, solutions rich in solvent were fractionated. The small fractionating column was used at total reflux, and pressure on the column was maintained at 760 mm. Only a few drops of distillate were withdrawn for analysis. The analytical procedure was identical to that used in analyzing samples from the equilibrium still.

Three samples were analyzed and the results averaged. Results of the two fractionations performed are presented in Table 1. This column is rather poorly insulated. When the first solution was fractionated, room temperature was about five degrees above the corrected temperature read on the column thermometer. When the 0.049 mole fraction solution was fractionated, room temperature was about two degrees below the corrected temperature read on the column thermometer.

Volume Change on Mixing.--Measurement of the volume change occurring on mixing trichloromonofluoromethane and bromine was not attempted, because the boiling point of the solvent was below room temperature. Large changes in temperature during measurement could not be permitted, for the effect of such changes on volume would render any results meaningless. It would be necessary, therefore, to carry out such measurements at the temperature of the surroundings. Air conditioning was not made available, because of the corrosive nature of bromine.

The System Bromine- 1,1-dichloro-2,2-difluoroethane

Operation of the Equilibrium Still.--Since the solvent used in this system boiled well above room temperature, and because equilibrium temperatures over the entire system varied through a small temperature range, no special difficulties were encountered. The procedure followed is that presented under General Procedure for Operating the Equilibrium Still. Dow-Corning silicone stopcock grease was sparingly used.

Method of Analysis.--The method of analysis followed for this system is identical to that presented under General Method of Analysis.

Results from the Small Fractionating Column.--From the data obtained from the equilibrium still, plotted on a vapor-liquid equilibrium diagram, the approximate composition of the azeotrope was obtained by interpolation. A mixture of very nearly this composition was volumetrically prepared, and fractionated at a pressure of 760 mm. Ice water was circulated through the condenser. After leaving the still at total reflux for some time, a small quantity of distillate was slowly drawn off at a high reflux ratio until the temperature became constant, and discarded. More than 25 ml of azeotrope was then slowly collected, and samples were analyzed at intervals. Before taking each sample, the column was run for a few minutes at total reflux and the pressure was checked. The column temperature remained constant while the 25 ml of azeotrope were collected. Three samples were analyzed and their average is recorded in Table 3. The reading of the column thermometer was corrected to 49.5° C.

As an additional check, the distillate collected from the small fractionating column as just described, was introduced into the equilibrium still. The boiling point of the azeotrope at 760 mm was then determined by means of thermocouple readings. From these readings, it appears that the boiling point is nearer 49.6° C than 49.5° C.

Test for Possibility of Reaction.--As mentioned in the introduction, the possibility that bromine would react with 1,1-dichloro-2,2-difluoroethane under these conditions, did not seem great. This possibility was checked, however, by the following procedure.

The refractive index of fraction number 8, from the purification

of this solvent (see Table 2 and Figure 3) was measured at 25° C and found to be 1.3769.

A solution consisting of 10 per cent bromine in fraction number 8, was volumetrically prepared and fractionally distilled in the large five-foot column. The azeotrope distilled over leaving clear solvent as the residue. The refractive indices after contact were determined from samples of liquid that condensed from the bottom of the fractionating column. The first liquid to condense after removing the distilling flask and replacing it with a clean flask, is sample #1 of Table 6, and had a refractive index of 1.3785. The second sample which condensed into another clean flask had a refractive index of 1.3773. It appears to follow from a study of Figure 3 that a third sample should approach the value 1.3769 even more closely, but no such sample could be obtained because of hold up by the column. At the end of the distillation the distilling flask was dry and contained a speck of charred solvent. Distillate from the top of the column still contained traces of bromine as indicated by the effect of a few drops on a starch-potassium iodide solution. Liquid condensing from the bottom of the column (samples #1 and #2 above) was free of bromine by this test.

Incidental to this test for reaction, three samples of the first few milliliters of distillate were analyzed and found to have a composition of 0.568 mole fraction bromine. Atmospheric pressure a few hours before making this analysis was 730.9 mm. This value then, should be a good estimate of the composition of the azeotrope formed by this system at 731 mm pressure.

Volume Change on Mixing.--The apparatus previously described was used for this determination. Care was taken to avoid mechanical loss on mixing, and the graduated cylinder was quickly stoppered after being filled. The volume of the mixture was read after several intervals of time, to assure that the mixture had returned to room temperature after the initial cooling effect. The quantities of solvent and bromine introduced into the cylinder were such that the resulting mixture had approximately the composition of the azeotrope. The per cent increase in volume on mixing for this system was found to be 1.8. Measurements were made to three significant figures, but due to loss by evaporation, precision beyond two significant figures was not obtained. This experiment was repeated several times and the individual results were averaged. The data for this determination are recorded in Table 7.

The System Bromine- 1,2,2-trichloro-1,1-difluoroethane

Operation of the Equilibrium Still.--The procedure followed is that presented under General Procedure for Operating the Equilibrium Still, with the exception that Dow-Corning silicone stopcock grease could not be used. This grease was dissolved by both pure solvent and its solutions. After making the first experimental run, grease from the stopcocks was found deposited at the lower end of the flash boiler. The solution used was discarded, and the still was cleaned with a potassium hydroxide-ethanol solution. Thereafter, no-lub stopcocks were used with no lubricant. Since the still was operated under about 20 mm pressure, these cocks leaked very slowly but continuously throughout each of the runs. The resulting pressure drop within the still was negligible be-

cause of the large capacity of the pressure tank, and because frequent adjustments were made to compensate for changes in atmospheric pressure. In making these runs it was necessary to introduce slightly more than the usual amount of solution into the equilibrium still. After equilibrium had been established, any excess was withdrawn to adjust the liquid level in the residue chamber to that level used in studying the other two systems.

No disadvantages resulted from this difficulty, except discomfort and danger to the operator. Ammonium hydroxide was placed a considerable distance from the delivery tubes to neutralize the escaping bromine vapor without contaminating the tubes.

Results from the Small Fractionating Column.--From the data obtained from the equilibrium still, plotted on a vapor-liquid equilibrium diagram, the approximate composition of the azeotrope was obtained by interpolation. A mixture of very nearly this composition was volumetrically prepared, and fractionated at a pressure of 760 mm. Ice water was circulated through the condenser. After discarding the first few milliliters of distillate, more than 30 ml of azeotrope was slowly collected, and samples were analyzed at intervals. Before taking each sample, the column was run for a few minutes at total reflux, and the pressure was checked.

A heavy vacuum lubricant was applied to the uppermost portion of the standard taper, male, ground-glass joint at the bottom of the column before attaching the distilling flask. It was hoped that vapor would not diffuse through the lower portion of the joint, to such an extent that the lubricant would be dissolved before distillation could be

completed. Such, however, was not the case. After analyzing two samples, it was necessary to disconnect the heating mantel, because of bromine vapor escaping into the room. Apiezon sealing wax was liberally applied around the joint, and distillation was continued. Two more samples were analyzed. The results of the best three analyses were averaged and found to be 0.747 mole fraction bromine.

Throughout the collection of the more than 30 ml of azeotrope, the column temperature remained constant. As a further check, the azeotrope was introduced into the equilibrium still, and its boiling point was determined by thermocouple readings. The corrected reading of the column thermometer, and the temperature reading obtained from the thermocouple agreed within a tenth of a degree. The boiling point obtained, 54.6° C, is recorded in Table 5.

Test for Possibility of Reaction.--The refractive index of the mixture of fractions 4 through 9 from the purification of this compound (see Table 4 and Figure 6) was measured at 25° C, and found to be 1.3900. This mixture of fractions was used in making solutions for all runs made with this system.

A solution consisting of 10 per cent bromine in the solvent was volumetrically prepared and fractionally distilled in the large five-foot column. The azeotrope distilled over leaving solvent as the residue. The refractive indices after contact were determined from samples of liquid that condensed from the bottom of the fractionating column. The first liquid to condense after removing the distilling flask and replacing it with a clean flask, gave a negative bromine test and had a refractive index of 1.3891. A second sample obtained in like manner also

gave a negative bromine test, and had a refractive index of 1.3899.

The distilling flask contained pale amber colored liquid. It might be mentioned here, that the original liquid as obtained from the manufacturer was amber colored before it was fractionated as indicated in Table 4. The first indication that this solvent would dissolve Dow-Corning stopcock grease, was discovered when a few drops of liquid from the distilling flask were dropped into a potassium iodide-starch solution. The stopcock grease floated to the liquid surface. It is suspected that most of this grease got into the distilling flask after it was removed from the column and covered with a beaker. Hot vapor condensing on the beaker ran over the greased, ground-glass joint, and thus into the flask. It was evident from the appearance of the grease film that much of it had dissolved.

The samples collected from the bottom of the column for the above test showed no indication of this amber color, and were apparently free of stopcock grease.

Volume Change on Mixing.---These measurements were made exactly as in the preceding system, so that the two would be comparable. The volumes of bromine and solvent that were mixed, were chosen so that the resulting mixture would have roughly the composition of the azeotrope in this system. The experiment was repeated four times, and the results averaged. Three of the individual results were in agreement to the third decimal place, but this precision is believed to be due to chance rather than accuracy. The per cent increase in volume was rounded off to the first decimal, and was found to be 0.3. The data for this determination are recorded in Table 7.

CHAPTER IV

DISCUSSION OF RESULTS

CHAPTER IV

DISCUSSION OF RESULTS

The System Bromine-Trichloromonofluoromethane.--Figure 1 is a plot of the equilibrium temperature vs. mole fraction bromine. The lower curve gives the composition of liquid that has atmospheric boiling points corresponding to points on the ordinate. The upper curve gives the composition of vapor that is in equilibrium with any liquid at its boiling point. It can be seen from this curve that the boiling point increases regularly as the mole fraction of bromine in the liquid is increased. No azeotrope is formed.

Figure 2 is a plot of mole fraction bromine in the vapor vs. mole fraction bromine in the liquid. The almost asymptotic approach of this curve to the diagonal is interesting. From the literature it was found that the vapor-liquid equilibrium diagram of the system ethyl alcohol-water has a very similar shape.

In Chapter III, it was mentioned that solutions rich in solvent were fractionated to assure the absence of an azeotrope in this system. Theoretically, any mixture of two liquids showing a regular increase in boiling point, can be separated into its components by fractional distillation. The data presented in Table 1, however, indicates that complete separation was not achieved, when solvent-rich mixtures were fractionated at total reflux in the small fractionating column.

This disappointing result should not be construed to indicate azeotrope formation, however, as will be explained. The first liquid

fractionated was previously separated in the equilibrium still into vapor that was 0.2 mole fraction bromine and liquid that was 0.4 mole fraction bromine, and is thus judged to have an over-all composition of about 0.3 mole fraction. When fractionated, this liquid produced distillate that was 0.064 mole fraction bromine. This result proves that no azeotrope exists between about 0.3 and 0.064 mole fraction bromine. Fractionation of the 0.049 mole fraction bromine solution similarly proved that no azeotrope is formed between 0.049 and 0.022 mole fraction bromine.

If McCabe and Thiele's method is applied to Figure 2, and if it is remembered that at total reflux the operating line coincides with the diagonal,¹¹ it is simple to count the number of theoretical plates necessary to achieve a given separation of the above solutions. By applying this method, it is evident that about three or four theoretical plates would be required to go from 0.3 to 0.064 mole fraction bromine or from 0.049 to 0.022 mole fraction bromine. The relatively large number of plates required for the latter small separation is due to the nearly asymptotic approach to the diagonal noted above. Separation becomes more difficult, for this reason, as the composition approaches that of pure solvent. It is very probable that the small column used, having a packed section of only about 40 centimeters in length, has no more than four theoretical plates. Incomplete separation, then is due not to the formation of an azeotrope, but to the fact that a fractionating column having a much larger number of theoretical plates would be

¹¹Badger and McCabe, Elements of Chemical Engineering, Second edition, (New York and London: McGraw-Hill Book Company, Inc., 1936), p. 357.

required for complete separation.

The fact that no azeotrope is formed in this system is not surprising. If the difference between the respective boiling points of the two components of a mixture is large, positive deviation from Raoult's law must be very large, in order that the total vapor pressure of some mixture may exceed the vapor pressure of the pure low-boiling component. The boiling point curve will not exhibit a minimum (azeotrope) unless the corresponding vapor pressure-composition curve has a maximum. The difference between the boiling points of trichloromonofluoromethane and bromine is 35.2 degrees centigrade.

There appears to be some evidence that azeotrope formation could possibly occur in this system, however. Using Hildebrand's method,¹² Spicer and Meyer¹³ found that the difference between the internal pressures of bromine and benzotrifluoride was 2740 atm. Even though the boiling point of benzotrifluoride is 45 degrees higher than that of bromine, an azeotrope is formed in the system bromine-benzotrifluoride. Using the same method, it was found that the difference between the internal pressure of trichloromonofluoromethane and bromine is 2786 atm. Since in the absence of hydrogen bonding the difference in the internal pressures of the components¹⁴ is an indication of the amount of deviation from Raoult's law to be expected, it appears¹⁵ to follow that this system is more likely to exhibit an azeotrope than is the system bromine-

¹²J. H. Hildebrand, *Solubility of Non-Electrolytes*, Second edition, (New York: Reinhold Publishing Corporation, 1936), pp. 98-106.

¹³Spicer and Meyer, *op. cit.*, p. 937.

¹⁴Ewell, Harrison and Berg, *loc. cit.*

¹⁵See page 29.

benzotrifluoride.

The likelihood of reaction between the solvent and bromine is very small, because the solvent is already saturated with halogens of higher electronegativity, whose carbon-halogen bond energies are larger than that of the carbon-bromine bond. The smoothness of the two equilibrium diagrams is also an indication that no reaction takes place. A test for reaction was not made, for pure solvent was not successfully separated from mixtures with bromine.

The System Bromine- 1,1-dichloro-2,2-difluoroethane.--Equilibrium diagrams for this system are presented in Figures 4 and 5. Figure 4 is a temperature-composition diagram corresponding to Figure 1, discussed above, and Figure 5 is a vapor composition-liquid composition diagram corresponding to Figure 2, above. It is evident from Figure 4 that this system exhibits a boiling point at 49.6° C, 9.2 degrees lower than the boiling point of the lowest-boiling pure component. At this boiling point minimum, both liquid and vapor have the composition 0.581 mole fraction bromine. In Figure 5 it is seen that the curve crosses the diagonal at this composition. Liquid mixtures of this kind, which distil unchanged at a definite temperature are called azeotropic mixtures.

That the boiling point depression at the azeotrope should be greater in this system than in the system following, is expected from the data presented in Tables 7 and 8. Since the boiling points of the components of this system differ only by 0.2 degrees, a very small positive deviation from Raoult's law should produce an azeotrope. The larger increase in volume on mixing, and greater cooling effect observed on mixing the components of this system, indicate that the positive

deviation from Raoult's law is larger than in the system following.

The difference in internal pressure between bromine and each of these solvents as calculated by Hildebrand's method,¹⁶ seems to be inconsistent with this larger deviation from Raoult's law. This difference was found to be 2340 atm for 1,1-dichloro-2,2-difluoroethane, and 2737 atm for 1,2,2-trichloro-1,1-difluoroethane. However, we must consider the effect of hydrogen bonding, which is usually more important than internal pressure differences.¹⁷ Both of these compounds probably form weak hydrogen bonds between adjacent molecules. There is ample evidence in the literature, indicating that weak hydrogen bond formation with the use of a hydrogen atom attached to a carbon atom of a halogenated hydrocarbon molecule can take place.¹⁸ For example pentachloroethane forms complexes with ether by hydrogen bonding. That this association between like molecules by hydrogen bonding is weak, is indicated by the fact that neither of these compounds is very soluble in water. Because $\text{CHCl}_2\text{CHF}_2$ contains two hydrogen atoms, and one of these hydrogen atoms is attached to a carbon atom that has two fluorine atoms attached to it, possibilities of hydrogen bond formation appear to be greater in this compound than it is in $\text{CHCl}_2\text{CF}_2\text{Cl}$. If this is true, more hydrogen bonds will be broken when bromine is introduced into this

¹⁶Hildebrand, loc. cit.

¹⁷Ewell, Harrison and Berg, loc. cit.

¹⁸S. Glasstone, Trans. Faraday Soc. 33, 200 (1937); D. B. McLeod and F. J. Wilson, Ibid., 31, 596 (1935); G. F. Zellhoefer, M. J. Copley, and C. S. Marvel, J. Am. Chem. Soc., 60, 1337 (1938); G. F. Zellhoefer and M. J. Copley, Ibid. 60, 1343 (1938).

solvent, than are broken when bromine is introduced into solvent of the following system. This breaking of hydrogen bonds, causes an increase in the partial molar volume and vapor pressure of the solvent in its mixtures, and therefore a positive deviation from Raoult's law. In the light of the possibility of hydrogen bonding, it is not surprising that increase in volume on mixing is greater with the components of this system, and that the boiling point depression at the azeotrope is larger in this system than in the system following.

The result of the test for reaction between the components of this system was not conclusive, but supports the contention that no reaction takes place. An examination of Table 6 and Figure 3, indicates that the refractive index of sample #1 was well within the range of higher-boiling fractions of $\text{CHCl}_2\text{CHF}_2$. It is evident that in separating solvent from its bromine mixture the solvent was fractionated, and sample #1, being taken from the last portion of liquid to leave the drying still pot, contained the highest boiling fraction of fraction number 8. That fraction number 8 should contain traces of higher boiling liquid is not unexpected. That the refractive index of sample #2, collected after removing only about two milliliters of liquid from the bottom of the column, was much closer to the refractive index of fraction number 8 before contact with bromine, is indication that only a trace of higher boiling liquid was present.

The smoothness of the equilibrium curve in Figures 4 and 5 is further indication that no reaction took place.

The System Bromine- 1,2,2-trichloro-1,1-difluoroethane.---Figures 7 and 8 are the equilibrium diagrams for this system. It can be seen from

Figure 7 that an azeotrope having a composition of 0.747 mole fraction bromine, and a boiling point of 54.6° C is formed in this system. In Figure 8, it can be seen that the vapor-composition vs. liquid-composition curve crosses the diagonal at 0.747 mole fraction bromine.

From the figures cited above for the system bromine-benzotrifluoride, it appears that azeotrope formation should be expected in this system. This system has a difference of only 13.0 degrees between the boiling points of the components, and a difference of 2737 atm between the estimated internal pressures. The system cited has a difference of 45.0 degrees between boiling points, and a difference of 2740 atm in internal pressures.

In making this comparison, it was noticed that the increase in volume on mixing benzotrifluoride and bromine as reported by Spicer and Meyer, was many times greater than the change in volume found with this system. Since the internal pressures of benzotrifluoride and 1,2,2-trichloro-1,1-difluoroethane are essentially the same, it follows that benzotrifluoride must be more highly associated than is the latter compound. The conclusion that benzotrifluoride molecules are associated will also explain the incorrect conclusion drawn in comparing the system bromine-trichloromonofluoromethane with the system bromine-benzotrifluoride on page 25. The benzotrifluoride molecules are probably attracted to each other through dipole association.

The result of the test for reaction between bromine and 1,2,2-trichloro-1,1-difluoroethane was not conclusive. This test indicates, however, that no reaction occurred. The argument is similar to that presented for absence of reaction between the components of the last

system. Inspection of Table 6 and Figure 6 shows that the refractive index of sample #1 was well within the range of the refractive indices of slightly higher-boiling fractions. In fact, the figure does not greatly differ from the refractive index of fraction number 9 of Figure 6. Fraction number 9 was included in the solvent mixed with bromine for this test. The refractive index of sample #2 differs from that of the original solvent within the range of experimental error. The indication is that the slight change observed in refractive index after contact with bromine, was due to further fractionation, and not to reaction between bromine and the solvent.

In general, the experimentally obtained results from all the systems studied are in accord with what might have been predicted from a consideration of the properties of these systems.

APPENDIX I

TABLES AND FIGURES

Table 1. Vapor-Liquid Equilibria Data for the System
Bromine-Trichloromonofluoromethane.

Temperature °C	Mole Fraction Bromine in Vapor	Mole Fraction Bromine in Liquid
23.6	0.000	0.000
23.7	0.022	0.031
28.1	0.249	0.506
29.2	0.292	0.597
34.8	0.416	0.823
39.6	0.520	0.911
41.2	0.563	0.925
50.5	0.804	0.977
58.8	1.000	1.000

Fractional distillation of a solution, which in the equilibrium still produced vapor that was 0.2 mole fraction bromine and liquid that was 0.4 mole fraction bromine, produced a distillate that was 0.064 mole fraction bromine. Using the same column, fractional distillation of 0.049 mole fraction bromine solution produced a 0.022 mole fraction distillate and a 0.119 mole fraction residue.

Table 2. Fractional Distillation of
1,1-dichloro-2,2-difluoroethane.

Fraction Number	Temperature °C (uncorr.)	Estimated Volume Distillate in ml	Refractive Index at 25° C
	52.9	0	_____
1	57.6	18	1.3773
2	58.0	34	1.3781
3	58.3	70	1.3779
4	58.4	104	1.3776
5	58.5	149	1.3772
6	58.6	183	1.3770
7	58.7	218	1.3769
8	59.0	252	1.3769
9	59.4	267	1.3772
10	59.9	297*	1.3879*
Liquid before fractionation			1.3780

The boiling point of fraction number 7 was determined in the equilibrium still at 760 mm pressure, and found to be 59.2° C. This value can be used to correct the uncorrected temperature readings given in this table.

*The residue in the distilling flask was added to fraction number 10 before these values were determined.

Table 3. Vapor-Liquid Equilibria Data for the System
Bromine- 1,1-dichloro-2,2-difluoroethane.

Temperature °C	Mole Fraction Bromine in Vapor	Mole Fraction Bromine in Liquid
59.0	0.000	0.000
57.0	0.113	0.046
54.4	0.246	0.123
53.7	0.293	0.154
51.2	0.447	0.307
50.0	0.559	0.509
49.9	0.565	0.542
49.7	0.578	0.567
49.6	0.581	0.581
49.8	0.622	0.691
51.0	0.702	0.825
52.2	0.762	0.893
55.5	0.882	0.972
58.8	1.000	1.000

Table 4. Fractional Distillation of
1,2,2-trichloro-1,1-difluoroethane.

Fraction Number	Temperature °C (uncorr.)	Estimated Volume Distillate in ml	Refractive Index at 25° C
	70.1	0	_____
1	70.9	17	1.3917
2	70.9	34	1.3910
3	71.0	67	1.3909
4	71.1	100	1.3908
5	71.1	133	1.3900
6	71.1	167	1.3899
7	71.2	200	1.3895
8	71.2	233	1.3894
9	71.2	268	1.3893
10	71.2	282	1.3892
11	71.2	291	1.3891
Drainage from fractionating column			1.3979

Table 5. Vapor-Liquid Equilibria Data for the System
Bromine- 1,2,2-trichloro-1,1-difluoroethane.

Temperature °C	Mole Fraction Bromine in Vapor	Mole Fraction Bromine in Liquid
71.8	0.000	0.000
70.0	0.085	0.026
63.6	0.359	0.163
57.8	0.553	0.342
56.5	0.638	0.479
55.2	0.722	0.641
54.6	0.747	0.747
55.1	0.805	0.834
56.5	0.903	0.949
58.8	1.000	1.000

Table 6. Data on Tests for Evidence of Reaction

Solvent	Fraction Number	Refractive Index at 25° C Before Contact with Br ₂	Refractive Index at 25° C After Contact with Br ₂
CHCl ₂ CHF ₂	8	1.3769	Sample #1, 1.3785 Sample #2, 1.3773
CHCl ₂ CF ₂ Cl	4 - 9	1.3900	Sample #1, 1.3891 Sample #2, 1.3899

Table 7. Data on Volume Changes Observed on Mixing.

Solvent	Temp. °C	Vol. of Bromine ml	Vol. of Solvent ml	Ideal Vol. of Mixture ml	Actual Vol. of Mixture ml	% Volume Increase
CHCl ₂ CHF ₂	29	1.71	2.25	3.96	4.03	1.8
CHCl ₂ CF ₂ Cl	31	2.37	1.60	3.97	3.98	0.3

Noticeable cooling occurred on mixing, and the effect appeared to be greater for CHCl₂CHF₂.

Table 8. The Physical Properties of the Components of the Systems Investigated.

Component	B.P. Obs. at 760 mm	Diff. in B.P.'s of Br ₂ and Solvent	Density (t ^o C)	Internal Pressure Estimate	Diff. in Estimated Internal Pressure of Br ₂ and Solvent
	^o C	^o C	gm/ml	atm	atm
Br ₂	58.8	—	3.119 (20) ^a	5417	—
			3.102 (25) ^b	5387	—
CCl ₃ F	23.6	35.2	1.494 (17.2) ^c	2631	2786
CHCl ₂ CHF ₂	59.0	00.2	1.494 (16.4) ^d	3077	2340
CHCl ₂ CF ₂ Cl	71.8	13.0	1.545 (25) ^e	2650	2737

^aInternational Critical Tables, (New York: McGraw Hill Book Company, 1928), III, p. 20.

^bLoc. cit.

^cF. Swarts, Ber., 26 Ref., 291 (1893).

^dF. Swarts, J. Chim. Phys., 20, 30 (1923).

^eA. L. Henne and E. C. Ladd, J. An. Chem. Soc., 58, 403 (1936).

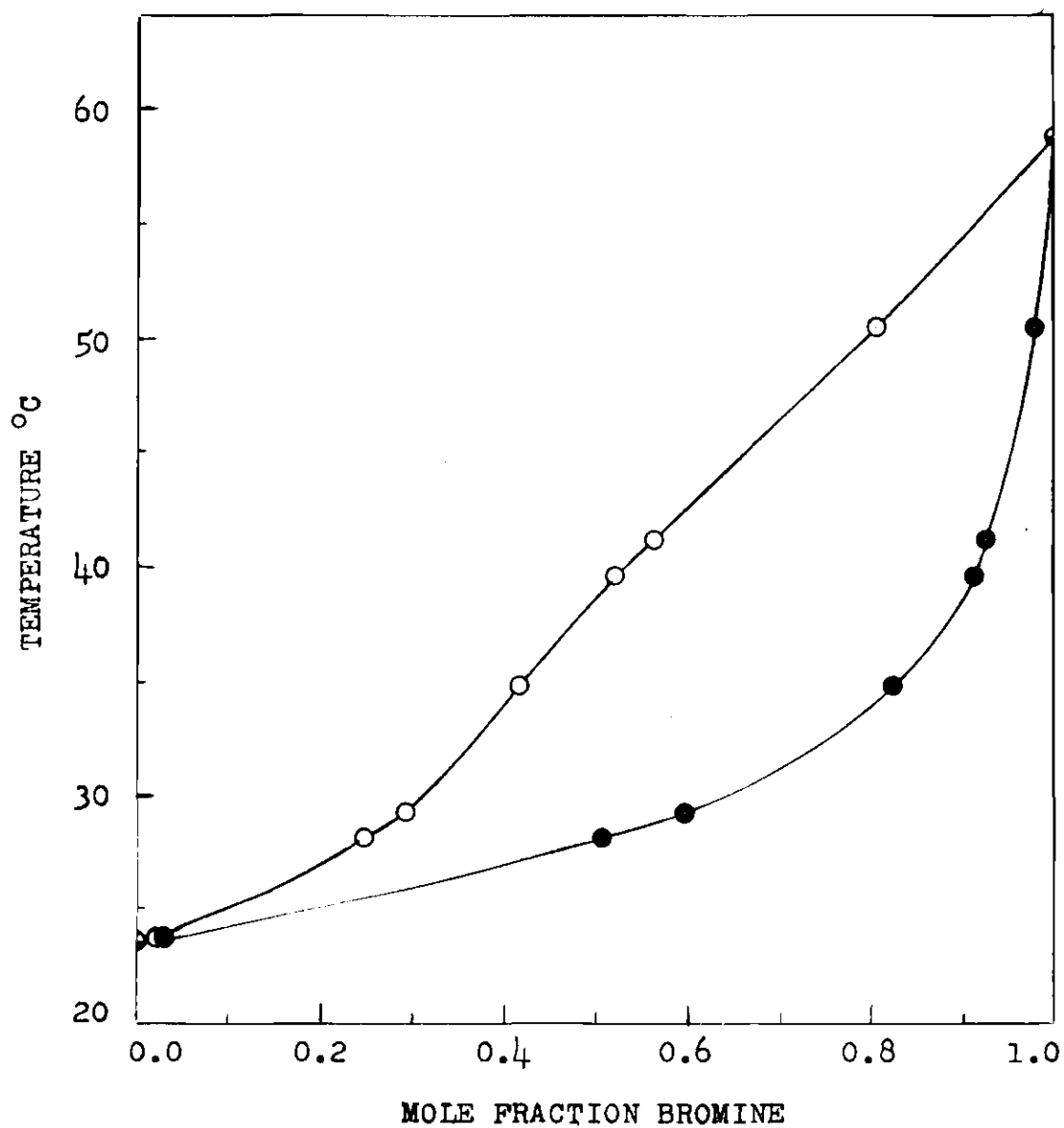


FIGURE 1

TEMPERATURE-COMPOSITION DIAGRAM FOR THE
SYSTEM $\text{Br}_2 - \text{CCl}_3\text{F}$ AT 760 mm PRESSURE

○ = VAPOR, ● = LIQUID
◐ = VAPOR AND LIQUID

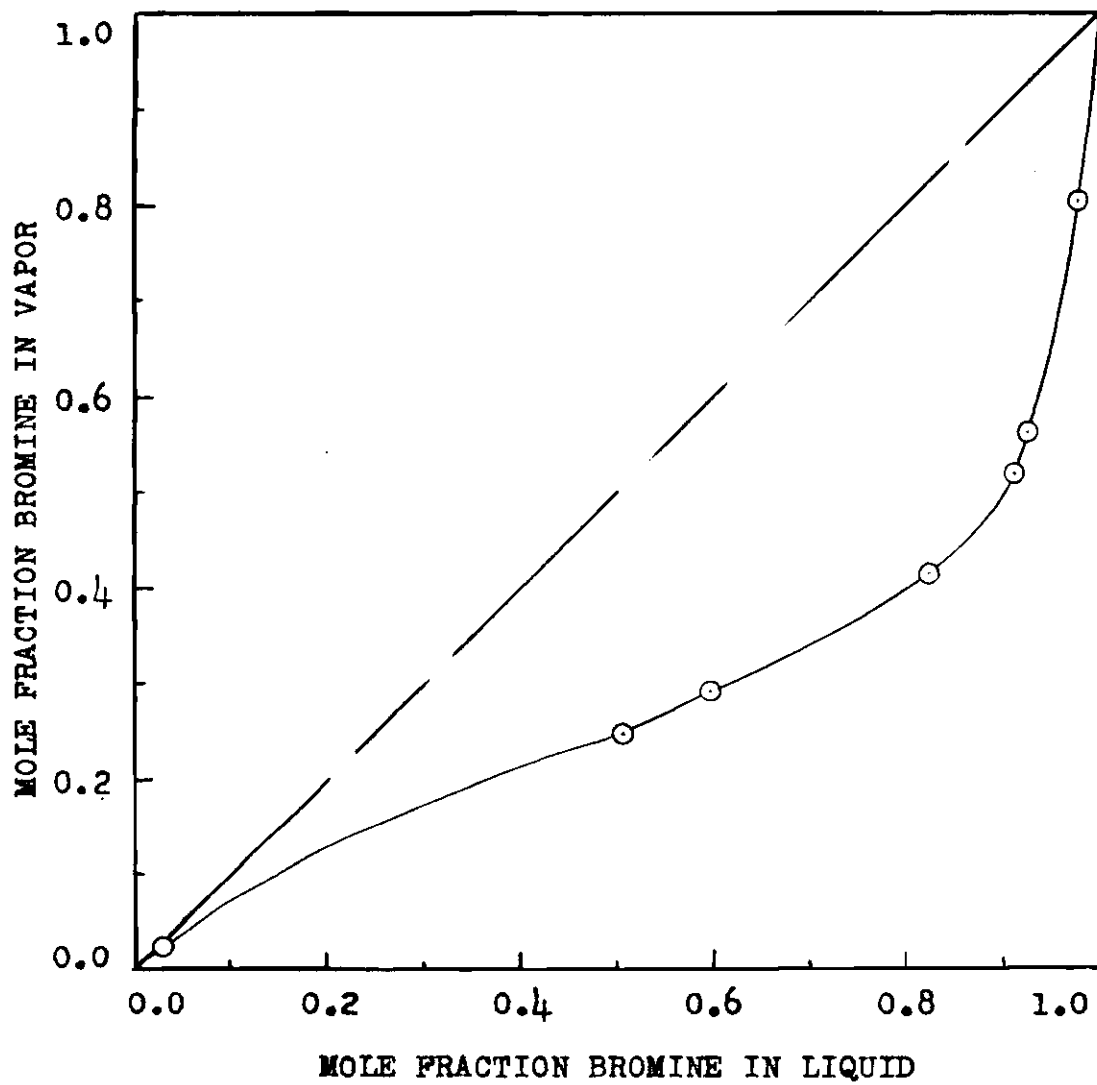


FIGURE 2

VAPOR-LIQUID EQUILIBRIUM DIAGRAM
FOR THE SYSTEM $\text{Br}_2 - \text{CCl}_3\text{F}$ AT
760 mm PRESSURE

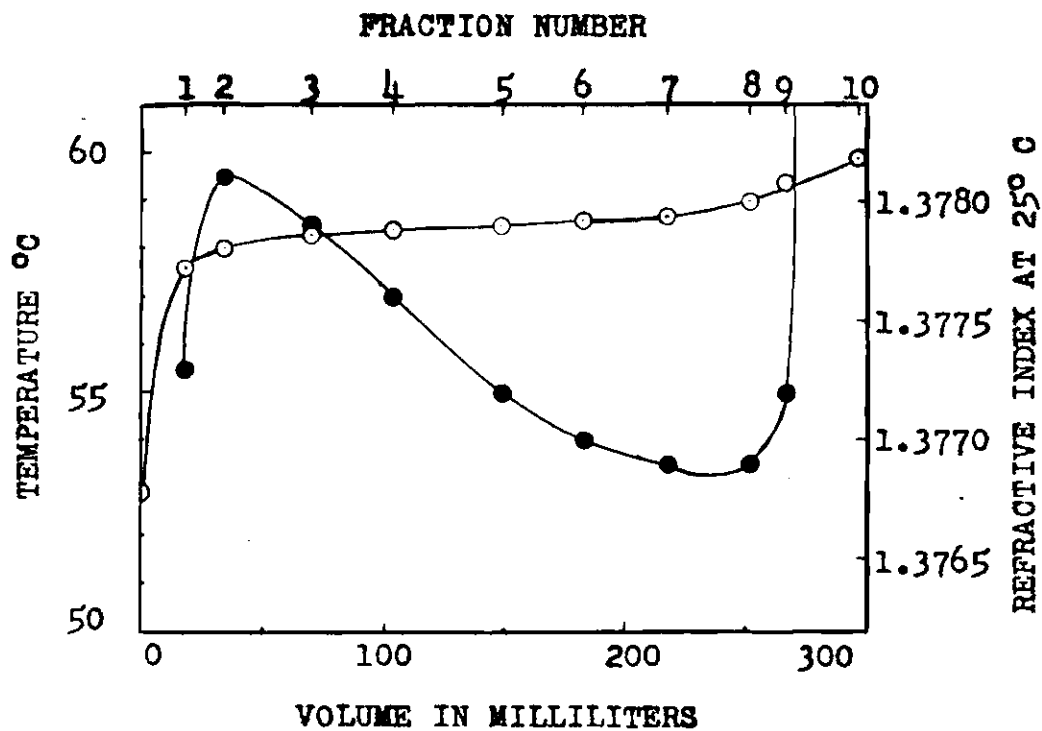


FIGURE 3

FRACTIONAL DISTILLATION OF $\text{CHCl}_2\text{CHF}_2$

○ = TEMPERATURE VS VOLUME
 ● = REFRACTIVE INDEX VS VOLUME

FRACTIONS 4, 5, 6, 7 AND 8 WERE USED IN THIS INVESTIGATION

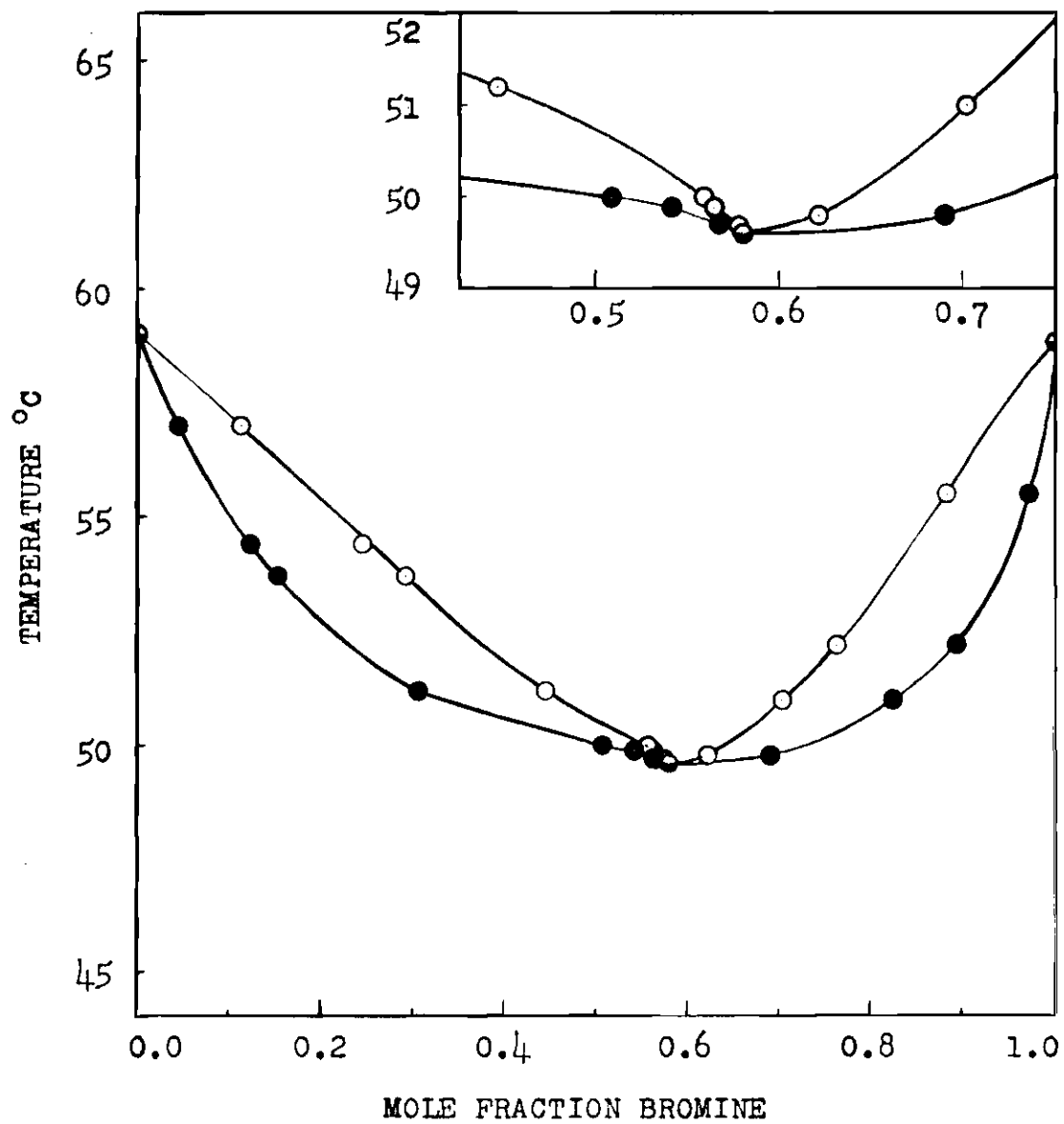


FIGURE 4

TEMPERATURE-COMPOSITION DIAGRAM FOR THE
SYSTEM $\text{Br}_2 - \text{CHCl}_2\text{CHF}_2$ AT 760 mm PRESSURE

○ = VAPOR, ● = LIQUID
● = VAPOR AND LIQUID

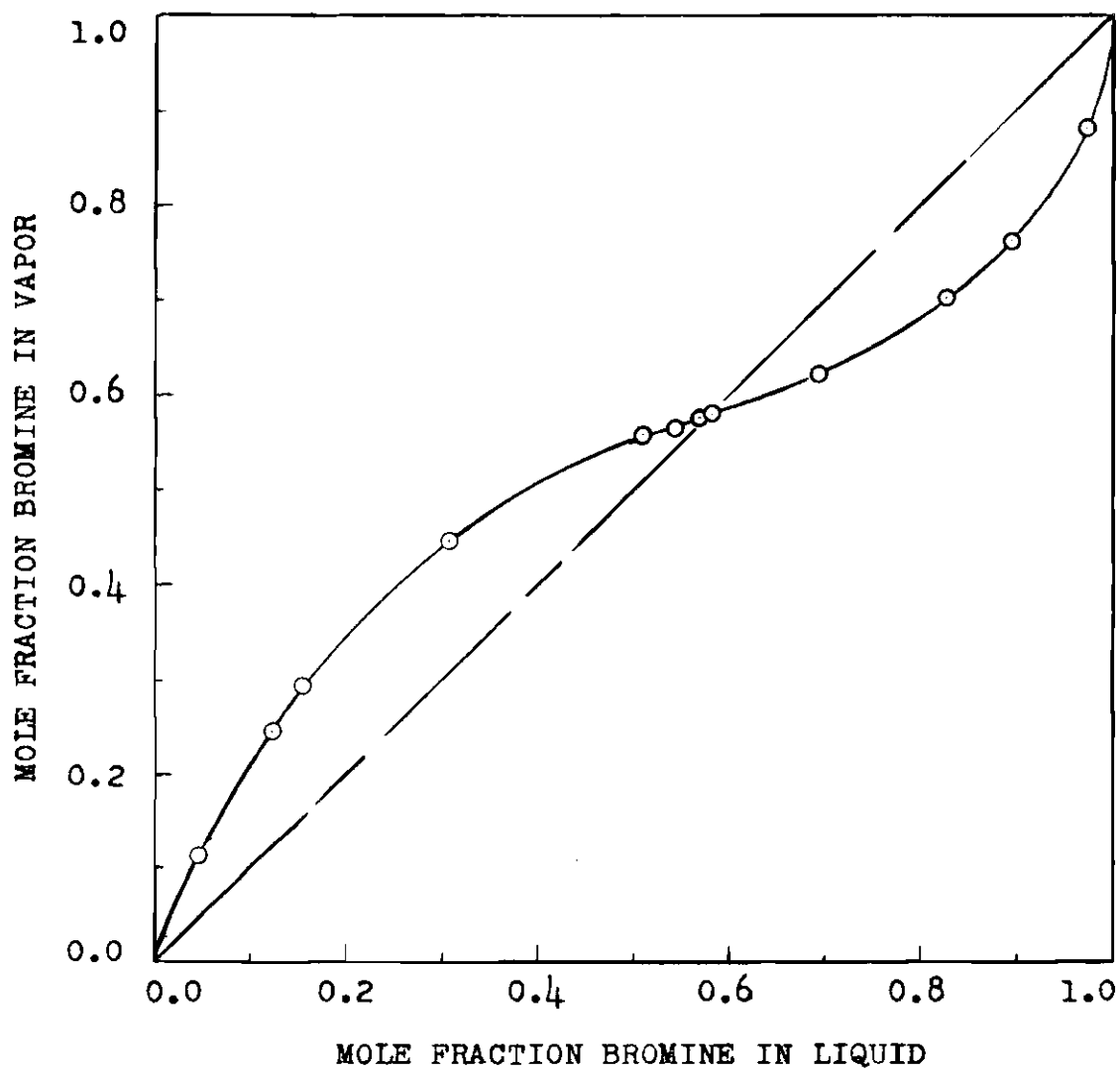


FIGURE 5

VAPOR-LIQUID EQUILIBRIUM DIAGRAM
FOR THE SYSTEM $\text{Br}_2 - \text{CHCl}_2\text{CHF}_2$
AT 760 mm PRESSURE

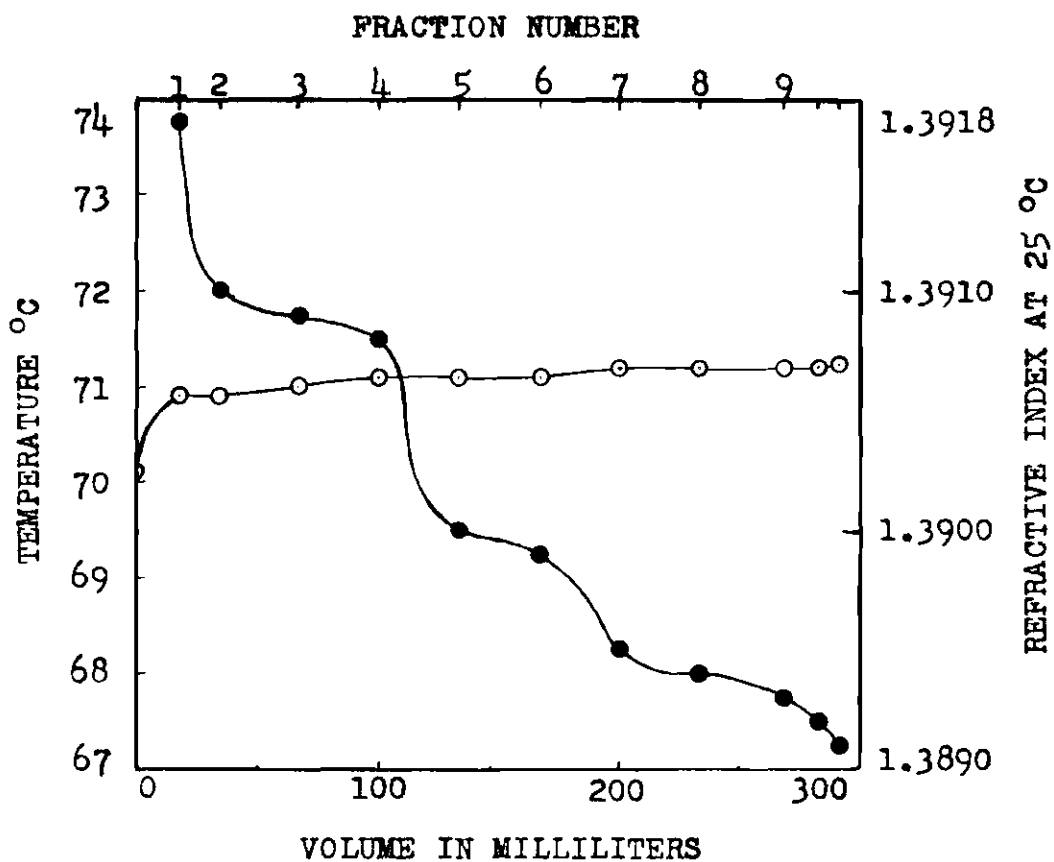


FIGURE 6

FRACTIONAL DISTILLATION OF $\text{CHCl}_2\text{CF}_2\text{Cl}$

- = TEMPERATURE VS VOLUME
 ● = REFRACTIVE INDEX VS VOLUME

FRACTIONS 4,5,6,7,8 AND 9 WERE USED IN THIS INVESTIGATION

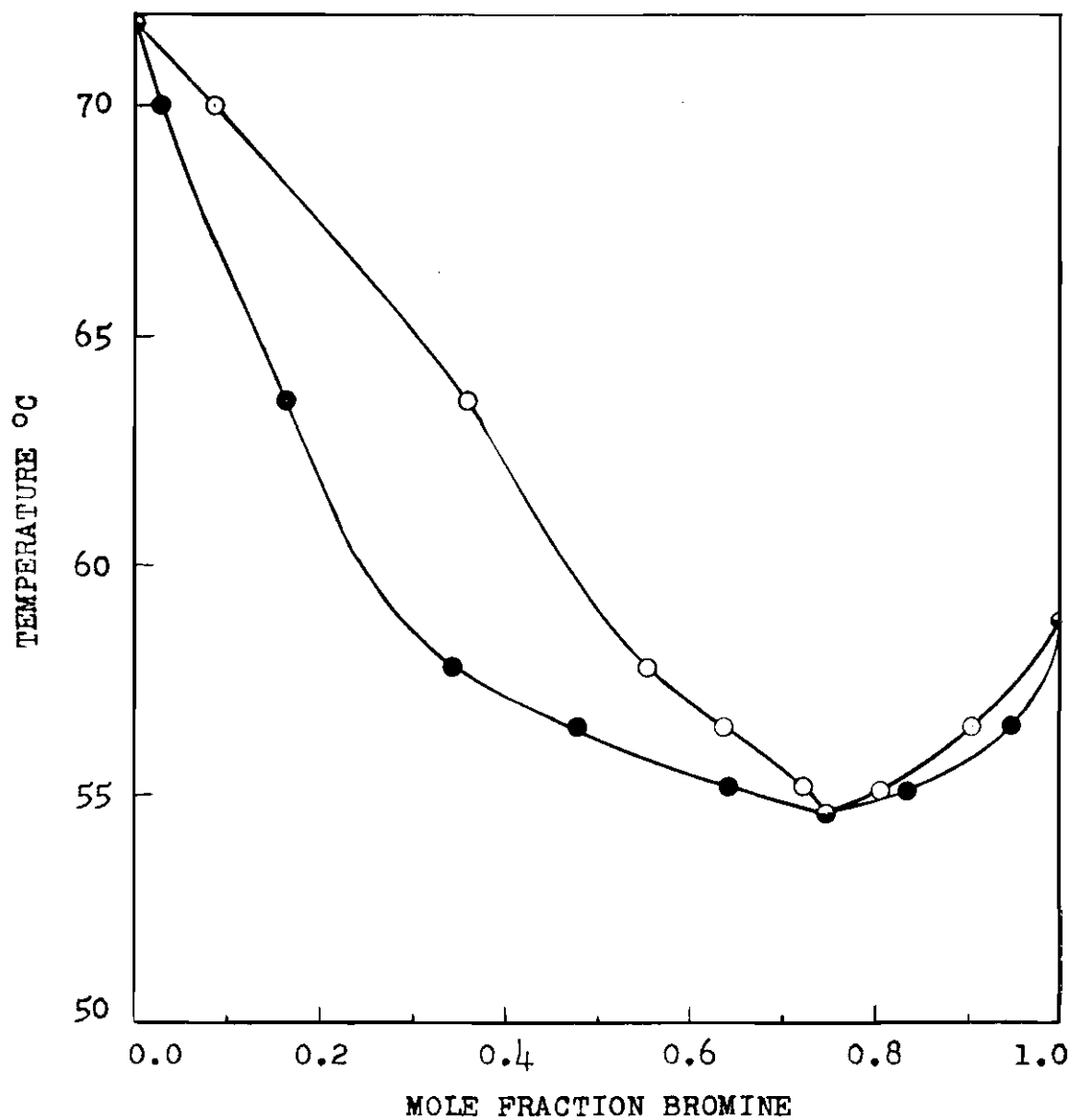


FIGURE 7

TEMPERATURE-COMPOSITION DIAGRAM FOR THE
SYSTEM $\text{Br}_2 - \text{CHCl}_2\text{CF}_2\text{Cl}$ AT 760 mm PRESSURE

○ = VAPOR, ● = LIQUID
◐ = VAPOR AND LIQUID

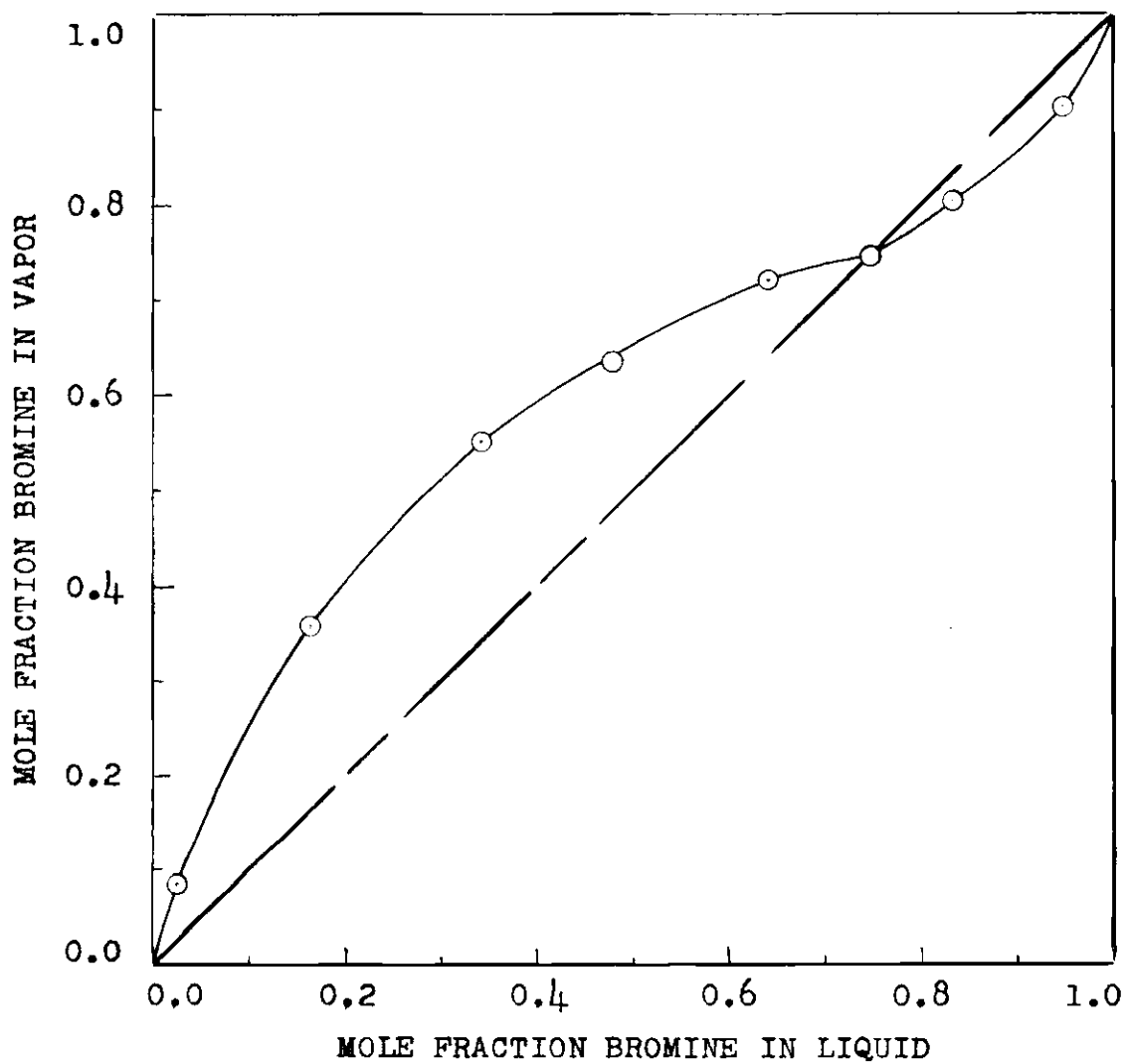


FIGURE 8

VAPOR-LIQUID EQUILIBRIUM DIAGRAM
FOR THE SYSTEM $\text{Br}_2 - \text{CHCl}_2\text{CF}_2\text{Cl}$
AT 760 mm PRESSURE

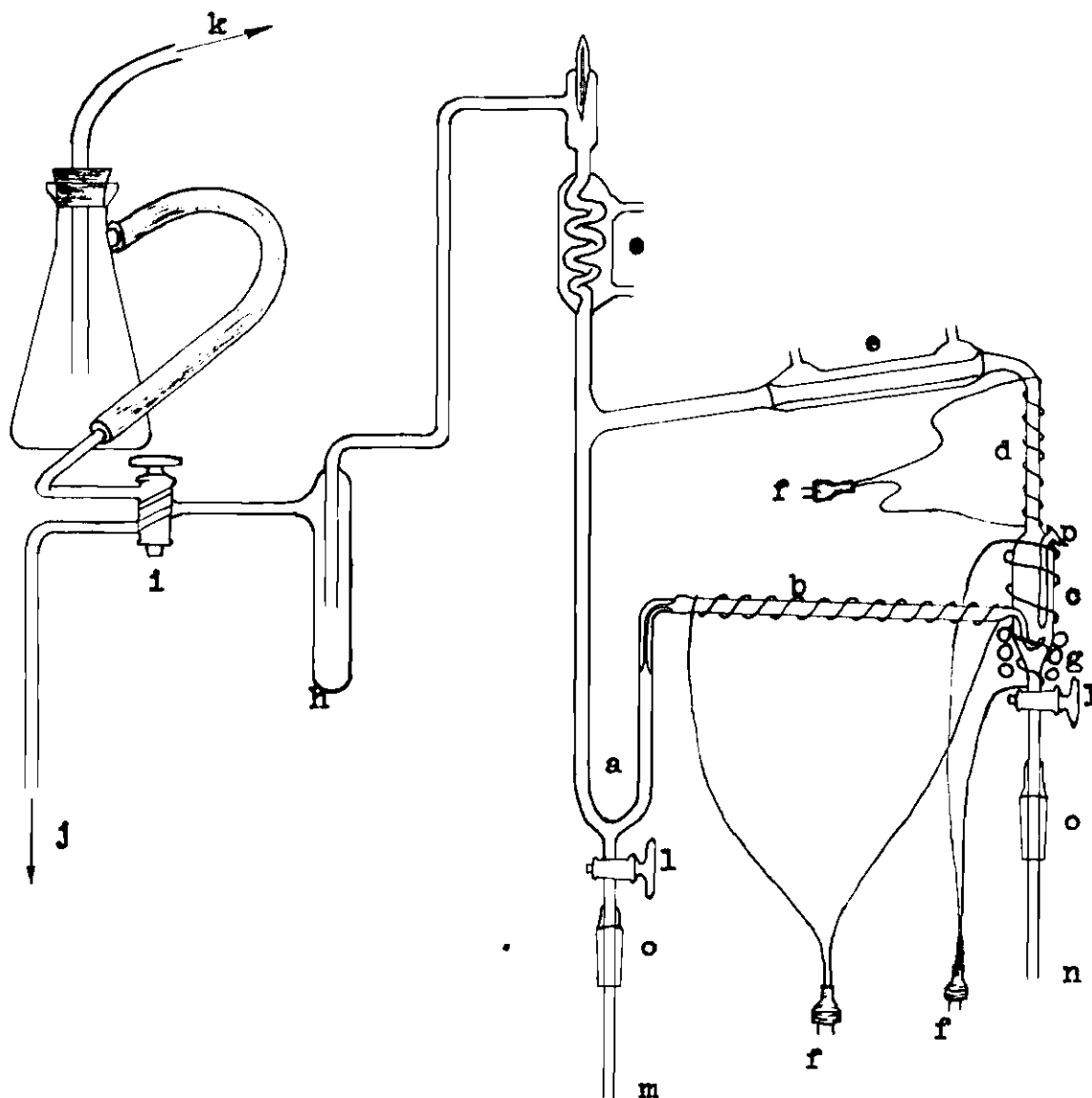


FIGURE 9

EQUILIBRIUM STILL

a DISTILLATE CHAMBER; **b** FLASH BOILER; **c** RESIDUE CHAMBER;
d VAPOR LINE; **e, e** CONDENSERS; **f, f, f** HEATING COILS; **g**
 COOLING COIL; **h** COLD TRAP; **i** TWO-WAY STOPCOCK; **j** TO PRESSURE
 TANK; **k** TO WATER ASPIRATOR; **l** NO-LUB STOPCOCKS; **m** DISTILLATE
 CHAMBER DELIVERY TUBE; **n** RESIDUE CHAMBER DELIVERY TUBE; **o,**
o STANDARD TAPER GROUND-GLASS JOINTS; **p** THERMOCOUPLE WELL

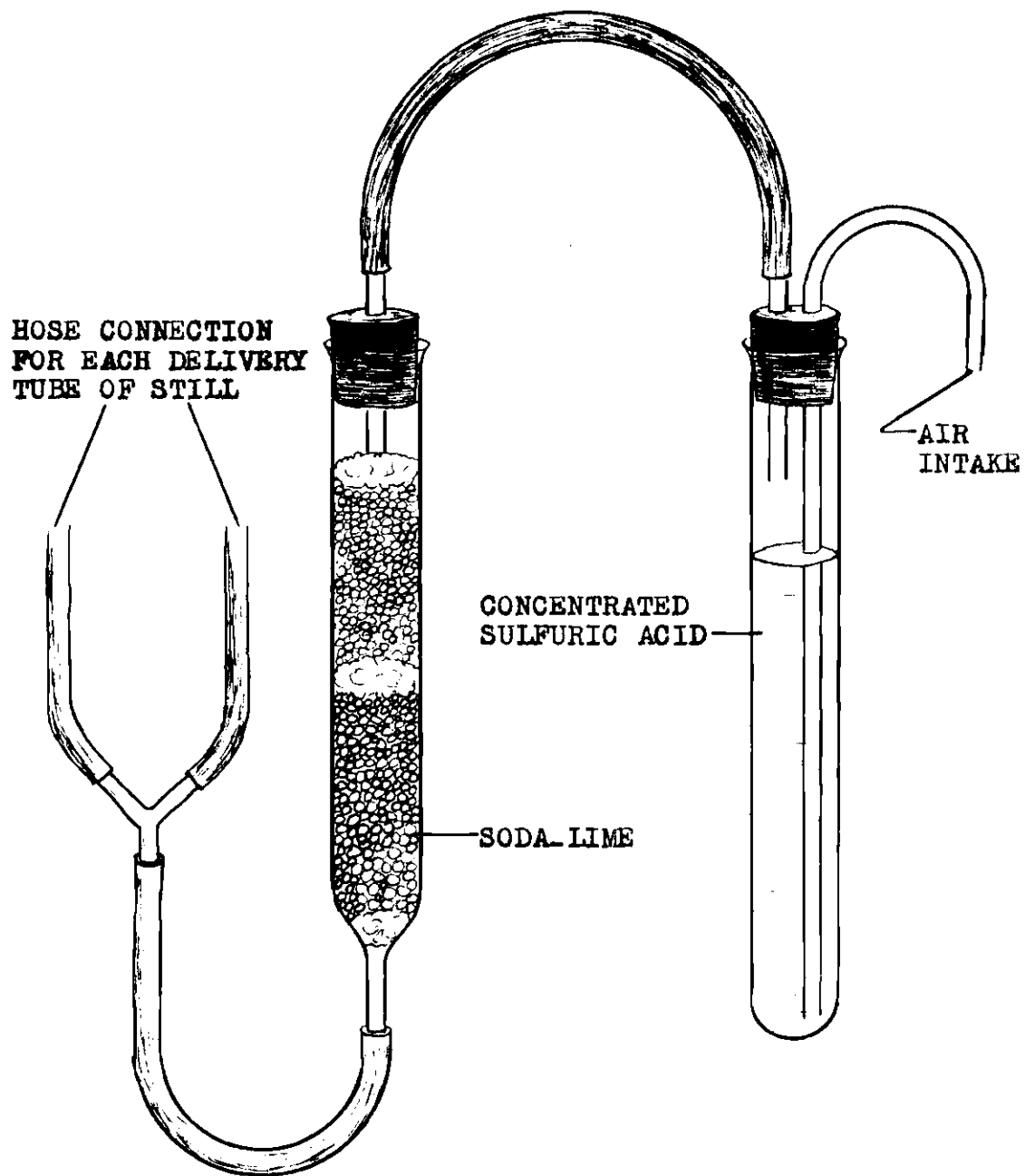


FIGURE 10

DRYING TRAIN

APPENDIX II

SAMPLE CALCULATIONS

APPENDIX II

SAMPLE CALCULATIONS

Analysis of a Sample

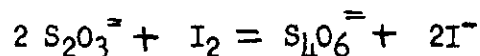
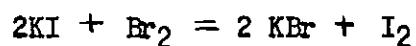
The calculations involved in making each analysis is demonstrated by the following example:

Data

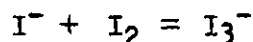
Weight of weighing bottle of KI solution —	14.4818 gm
Weight of weighing bottle and KI solution + sample —	15.2052 gm
Weight of sample —	0.7234 gm
Milliliters of 0.2012 N $\text{Na}_2\text{S}_2\text{O}_3$ standard solution to titrate the sample —	14.84 ml

Calculation

The reactions involved are:



A large excess of KI was maintained to reduce the volatilization of iodine by the formation of tri-iodide ions:



From the second equation it can be seen that the equivalent weight of iodine is one atomic weight. From the first equation it is evident that one atomic weight of iodine is equivalent to one atomic

weight of bromine. It follows then, that the equivalent weight of bromine is its atomic weight.

$$\begin{aligned} \text{Equivalent weights of bromine} &= \text{Normality of Na}_2\text{S}_2\text{O}_3 \text{ solution} \\ &\times \frac{\text{Milliliters of Na}_2\text{S}_2\text{O}_3}{1000} \\ &= 0.2012 \times \frac{11.84}{1000} = 0.002986 \end{aligned}$$

$$\begin{aligned} \text{Moles of bromine} &= 1/2 \times \text{Equivalent weights of bromine} \\ &= 1/2 \times 0.002986 = 0.001493 \end{aligned}$$

$$\begin{aligned} \text{Weight of bromine} &= \text{Equivalent weights of bromine} \times \\ &\quad \text{Equivalent weight of bromine} \\ &= 0.002986 \times 79.92 = 0.2386 \text{ gm} \end{aligned}$$

$$\begin{aligned} \text{Weight of CHCl}_2\text{CHF}_2 &= \text{Weight of sample} - \text{Weight of bromine} \\ &= 0.7234 - 0.2386 = 0.4848 \text{ gm} \end{aligned}$$

$$\begin{aligned} \text{Moles CHCl}_2\text{CHF}_2 &= \frac{\text{Weight of CHCl}_2\text{CHF}_2}{\text{Molecular weight of CHCl}_2\text{CHF}_2} \\ &= \frac{0.4848}{134.9} = 0.003593 \end{aligned}$$

$$\begin{aligned} \text{Total moles} &= \text{Moles of bromine} + \text{Moles of CHCl}_2\text{CHF}_2 \\ &= 0.001493 + 0.003593 = 0.005086 \end{aligned}$$

$$\begin{aligned} \text{Mole fraction bromine} &= \frac{\text{Moles of bromine}}{\text{Total moles}} \\ &= \frac{0.001493}{0.005086} = 0.294 \end{aligned}$$

Determination of Change in Volume on Mixing

Data

Volume of bromine added --	1.71 ml
Volume of $\text{CHCl}_2\text{CHF}_2$ added --	2.25 ml
Actual volume of mixture --	4.03 ml

Calculation

$$\begin{aligned}\text{Ideal volume of mixture} &= \text{Volume of bromine} + \text{Volume of } \text{CHCl}_2\text{CHF}_2 \text{ added} \\ &= 1.71 + 2.25 = 3.96\end{aligned}$$

$$\begin{aligned}\text{Volume increase} &= \text{Actual volume of mixture} - \text{Ideal volume of mixture} \\ &= 4.03 - 3.96 = 0.07 \text{ ml}\end{aligned}$$

$$\begin{aligned}\text{Per cent volume increase} &= \frac{\text{Volume increase}}{\text{Ideal volume of mixture}} \times 100 \\ &= \frac{0.07}{3.96} \times 100 = 1.8\end{aligned}$$

Estimation of Internal Pressure¹⁹DataSolvent -- $\text{CHCl}_2\text{CF}_2\text{Cl}$ Observed boiling point of solvent at 760 mm -- 71.8°C Density of solvent at 25°C -- 1.545 gm/mlCalculation

$$\begin{aligned}\text{Energy of vaporization} &= \Delta E_v = 5280 + (24.5 \times \text{atmospheric boiling} \\ &\quad \text{point in } ^\circ \text{C})\end{aligned}$$

$$= 5280 + (24.5 \times 71.8) = 7039 \text{ cal}$$

$$\text{Molar volume at } 25^\circ \text{C} = v = \frac{\text{Molecular weight}}{\text{Density at } 25^\circ \text{C}}$$

$$= \frac{169.4}{1.545} = 109.7 \text{ ml}$$

¹⁹Hildebrand, loc. cit.

$$\text{Internal pressure } \frac{\Delta E_v}{V} = \frac{7039}{109.7} = 64.19 \text{ cal/ml}$$

$$64.19 \frac{\text{cal}}{\text{ml}} \times 41.29 \frac{\text{ml} \cdot \text{atm}}{\text{cal}} = 2650 \text{ atm}$$

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