VAPOR-LIQUID EQUILIBRIA STUDIES OF BROMINE AND

SUITABLE BROMINE SOLVENTS

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Leon Herbert Meyer

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VAPOR-LIQUID EQUILIBRIA STUDIES OF BROMINE AND

SUITABLE BROMINE SOLVENTS

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CHAPTER I

INTRODUCTION

As a continuation of an investigation,[1] started previously, to

discover binary azeotropes consisting of one colored and one colorless

component, it was decided to study further possibilities in systems

of bromine and colorless bromine solvents. Azeotropes of this general

type are valuable in the study of the methods employed to separate

azeotropic mixtures, since such separation can be observed merely by

inspection.

The choice of inert bromine solvents was difficult due to the

high reactivity of bromine itself. The number of these solvents was

further limited by the boiling point range of these liquids for which

azeotrope formation with bromine was deemed even feasible. Spicer and

Kruger[1] investigated the system bromine-carbon tetrachloride and proved

the existence of an azeotrope in this system. Hence, it was decided to

study first, systems composed of other completely halogenated saturated

hydrocarbons and bromine. To go higher in this series, however, it was

necessary to use fluorine containing compounds in order that the boiling

points should not be excessively high. Vapor-liquid equilibria studies

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[1]W. M. Spicer and J. Kruger, J. Am. Chem. Soc., 72, 1855-56
(1950).

were run on three systems of this type; viz., bromine -- 1,1,2-trifluoro-1,2,2-trichloroethane, bromine -- 1,1,1,2-tetrachloro-2,2-difluoroethane, and 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane.

Also, due to the stabilizing effect given to aromatic hydrocarbons by the trifluoromethyl group, it was deemed possible that in the absence of a catalyst a compound such as benzotrifluoride (trifluoromethyl benzene) might serve as an inert solvent for bromine. Such was found to be the case for the system bromine-benzotrifluoride; and therefore a similar investigation was conducted for this system.

The final system studied consisted of bromine and carbon disulfide, a commonly used solvent for bromine.

The detailed report on the procedures employed for the vapor-liquid equilibria studies for these five systems and the results obtained will be given in the ensuing chapters.

CHAPTER II

THEORETICAL DISCUSSION

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1. Ideal Solutions

An ideal solution is generally defined as one which obeys Raoult's law for all concentrations and at all temperatures and pressures. Raoult's law states that at any temperature the partial pressure, p_i, of any constituent in a liquid solution is equal to the product of the mole fraction, N_i, of that component in the solution, and the vapor pressure of the component in its pure state, p_i°, at the same temperature; i. e.,

$$p_i = N_i \, p_i^\circ.$$

For the statement of the law thermodynamically, it is customary to replace partial pressures by fugacities, f, in order to remove the requirement that the vapors behave as ideal gases, thus,

$$f_i = N_i \, f_i^\circ.$$

Actually, Raoult's law is strictly adhered to only by a highly limited number of liquid mixtures (e. g. solutions of isotopes or of optical isomers). In many instances, however, adherence to it is so closely approached (e. g. benzene and toluene, hexane and heptane) that for all practical purposes, such solutions are considered ideal. This close approximation to ideality generally is found in mixtures of liquids similar in chemical composition, whose intermolecular forces

and molar volumes do not greatly differ.[1]

For ideal solutions the following relationships can be thermo-dynamically proved:[2]

$$\text{(a)} \quad \left[\frac{\partial \ln (f_i/f_i^\circ)}{\partial T} \right]_{P,N} = \frac{H_i^\circ - \overline{H}_i}{RT^2} = 0$$

$$\text{(b)} \quad \left[\frac{\partial \ln (f_i/f_i^\circ)}{\partial P} \right]_{T,N} = \frac{\overline{V}_i - V_i^\circ}{RT} = 0$$

$$\text{(c)} \quad \left[\frac{\partial \left(\frac{\partial P}{\partial T} \right)_V}{\partial \ln N_i} \right]_{T,P} = 0$$

where H_i° = molar heat content of component in pure state

$\overline{H}_i$ = partial molar heat content of component in solution

V_i° = molar volume of component in pure state

$\overline{V}_i$ = partial molar volume of component in solution

From (a) it is thus seen that no heat change can result from mixing the constituents of an ideal solution. Similarly relationship (b) states that there can be no accompanying volume change. The expression in (c) asserts in effect that only those liquids having identical values of the thermodynamic quantity $\left(\frac{\partial P}{\partial T} \right)_V$ can form completely ideal solutions.

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[1] W. H. Rodebush, An Introductory Course in Physical Chemistry, Second edition, (New York: D. Van Nostrand Company, 1938), p. 154.

[2] J. H. Hildebrand, Solubility of Non-Electrolytes, Second edition, (New York: Reinhold Publishing Corporation, 1936), pp. 56-64.

2. Non-ideal Solutions

When solutions do not exhibit behavior in compliance to Raoult's law, they are termed non-ideal. The deviation from Raoult law behavior can be either positive or negative; i. e.,

(1) Positive deviation: $f_i > N_i f_i°$.

(2) Negative deviation: $f_i < N_i f_i°$.

Positive deviations are, by far, more common than negative ones.

Considering the usual experimentally observed behavior of non-ideal solutions with variation of temperature and pressure and using the relations (a) and (b) given in the preceding section, it can be shown that the mixing of the components of a non-ideal solution is ordinarily accompanied by changes in the heat content and volume. Furthermore, it is generally true that for systems exhibiting positive deviation from ideal behavior, mixing of the constituents results in an absorption of heat and an increase in volume, while just the opposite is observed in the case of negative deviation. The extent of these thermal and volume changes is an indication of the degree of non-ideality of the solution.

A better and in a sense more quantitative indication of the extent of deviation from ideal behavior which would be expected of various systems can be obtained from relation (c) given in the preceding section. Since only liquids having identical values of the quantity $\left(\frac{\partial P}{\partial T}\right)_V$ can be expected to form completely ideal solutions, it would be reasonable to assume that the amount by which the value of this quantity for two liquids differs would be at least a semi-quantitative indication of the degree of non-ideality. From one of the thermodynamic equations of state,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right].$$

The thermodynamic quantity $\left(\frac{\partial E}{\partial V}\right)_T$, known as the "internal pressure," is a good measure of the balance existing between intermolecular attractive and repulsive forces.[3] For most liquids, the order of magnitude of the internal pressure is about 10^3 atmospheres; thus under ordinary conditions, the external pressure, P, is totally neglible in the above relationship. Therefore, to an excellent approximation,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T,$$

or at constant temperature,

$$\left(\frac{\partial P}{\partial T}\right)_V = k\left(\frac{\partial E}{\partial V}\right)_T.$$

Thus, at low pressures the internal pressure differences existing between liquids is seen to be a good measure of the non-ideality of solutions.

Several methods are available for determining, or at least estimating, internal pressure of liquids. One relationship derivable from the van der Waals equation is,

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2} \quad [4]$$

where a = van der Waal constant

V = molar volume

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[3]Ibid., p. 99.

[4]S. Glasstone, Thermodynamics for Chemists, (New York: D. Van Nostrand Company, 1947), p. 159.

Hildebrand[5] gives another method of approximating internal pressures, which was particularly useful in this investigation due to the lack of information on the physical properties of most of the liquids studied. Employing his method, internal pressures for non-polar or nearly non-polar liquids can be approximated by the relationship,

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{\Delta E_V}{V}$$

where ΔE_V = energy of vaporization

V = molar volume

An empirical expression given by Hildebrand for estimating the energy of vaporization at 25° C in calories is given as follows:

$$\Delta E_V = 5280 + 24.5\ t_b$$

where t_b = atmospheric boiling point in $^\circ$ C

The factors which cause deviation from ideal behavior are those factors which tend to effect a change in the environmental forces existing around the molecules of the liquids. In a broad classification, these changes are two-fold -- those originating from an alteration in the so-called van der Waals force fields (including polarity effects) existing around the molecules and those arising from solvation between unlike molecules or a decrease in the association between like molecules. Ewell, Harrison, and Berg[6] have stated that the non-ideality of solutions

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[5]Hildebrand, op. cit., pp. 98-106.

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

is a function of the effects of hydrogen bonding and difference in internal pressures, the former being by far the more important. According to this source, hydrogen bonding is possible between donor atoms -- fluorine, oxygen, or nitrogen -- and "active" hydrogen acceptor atoms, the "active" designating hydrogen atoms attached to nitrogen, oxygen, or fluorine atoms or to carbon atoms to which is also attached at least one nitro, cyano, or halogen group.

3. Partial Miscibility

If the positive deviation from ideality for a mixture of two liquids is sufficiently great, the liquids will not be miscible in all proportions. In such cases two liquid layers will be formed whenever a specific concentration of one component in the other is exceeded. Since the extent of non-ideality is generally a function of the temperature, the degree of immiscibility will change with changes in temperature. Usually such systems approach total miscibility as the temperature is increased, although in a few cases due to other factors, the reverse is true.[7] Frequently, it is found that above a certain temperature, designated the upper consolute temperature, the two liquids become miscible in all proportions. However, in many instances, before this temperature is reached, the combined vapor pressure of the two liquids becomes sufficiently high to cause boiling, and thus at that pressure there is no temperature at which the liquids are completely miscible.

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[7]S. Glasstone, The Elements of Physical Chemistry, (New York: D. Van Nostrand Company, 1946), p. 360.

4. Azeotropes

Often there occurs in the plot of total vapor pressure vs. composition a maximum, in the case of positive deviation, or a minimum, in the case of negative deviation. In this event, there results for the mixture of this composition a boiling point lower, if the deviation is positive, or higher if negative, than that of any mixture of different composition. Moreover, this type of mixture will distill without change in composition; i. e., the equilibrium liquid and vapor phases have identical analyses. Such a mixture is termed a constant boiling mixture or an azeotrope.

According to Ewell, Harrison, and Berg[8] the formation of azeotropes depends upon the non-ideality of the solutions and the difference in boiling points existing between the components. The possibility that a system will exhibit azeotropic phenomenon is lessened as boiling point difference increases and as deviation from ideality decreases. One other determining factor is external pressure. Changes in applied pressure due to different rates of change of the boiling points of the two components with pressure usually cause a shift in the azeotropic concentration as well as a change in the azeotropic boiling point. Examples can be cited of systems in which azeotropic behavior is exhibited at some pressures, but not at others.[9]

If, in the case of partially miscible liquids, two liquid layers exist at the azeotropic boiling point over a range of concentrations,

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[8]Ewell, Harrison, and Berg, loc. cit.

[9]E. C. Britton, H. S. Nutting, and L. H. Horsley, Anal. Chem., 19, 601-2 (1947).

the azeotrope formed is termed a two-phase azeotrope. As long as two liquid phases are present, the liquid mixture will exhibit the azeotropic boiling point and will be in equilibrium at that temperature with a vapor of the azeotropic composition.

5. Application of Concepts to Systems Studied

In Table VIII are recorded the data required for consideration of the systems studied for this investigation, in the light of the concepts discussed above. The estimates of internal pressures, all calculated by use of the Hildebrand method (discussed in Section 2 of this chapter) in order that the comparison remain on the same basis, are listed. Also, the molar volumes and the boiling points observed at 760 mm are given.

Since no hydrogen bonding is possible among the components of any of the systems, the internal pressure differences and the differences in molar volumes are the important indications of the deviations from ideality to be expected. From an examination of Table VIII the system bromine-carbon disulfide would be expected to approximate most closely an ideal mixture, while the system bromine — 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane would be expected to exhibit the largest deviation from ideal behavior. The other three systems studied lie between these extremes.

In predicting the formation of minimum boiling azeotropes (Maximum boiling azeotropes result almost exclusively from the effects of hydrogen-bond formation, impossible in the systems studied.), the system bromine — 1,1,2-trifluoro-1,2,2-trichloroethane appears to be the most favorable for the exhibition of this phenomenon, due to its

relatively large difference in internal pressure, 3170 atms, and its

comparatively small difference in boiling points, 11.3° C. In all the

systems, however, with the exception of bromine-carbon disulfide, due to

large internal pressure and molar volume differences, azeotrope formation

appears to be a definite possibility, in spite of the large boiling point

differences existing in two of the systems.

6. Possibility of Reactions between Components

In order for any vapor-liquid equilibria studies on liquid

mixtures to have validity, it is essential that no reaction take place

between the constituents of the system. Thus, due to the unusually high

reactivity of bromine, it is necessary to examine the information avail-

able, for the likelihood of the occurrence of a reaction between the

components of each system.

In the case of the three systems involving bromine and the

saturated fluorochlorocarbons, reaction between constituents seems

highly improbable. Simons[10] has cited the very great stabilizing effects

of the -CF_3 group and the general inertness imparted to organic compounds

by fluorine substituents; also Grosse and Cady[11] have cited the high

stability of saturated fluorocarbons toward bromine. Brice, Pearlson,

and Simons[12] report that bromine reacts with saturated fluorocarbons

in the vapor phase at temperatures ranging from about 900° C for C_2F_6

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[10] J. H. Simons, Ind. Eng. Chem., 39, 240 (1947).

[11] A. V. Grosse and G. H. Cady, Ind. Eng. Chem., 39, 368 (1947).

[12] T. J. Brice, W. H. Pearlson, and J. H. Simons, J. Am. Chem. Soc., 71, 2499-501 (1949).

to about 800° C for C_5F_{12}. At temperatures as high as 820° C, bromine gives little indication of reacting with C_3F_8. Reaction with C_3F_7Cl takes place at 852° -70° C. McBee and co-workers[13] have reported that even the substitution reaction of bromine for hydrogen in certain fluoro-hydrocarbons proceeds at a very slow rate below 400° C.

With the system bromine-benzotrifluoride, a substitution reaction, bromine for hydrogen, must, of course, be considered. At moderately low temperatures and in the absence of a catalyst, however, there would appear to be a good possibility that no reaction would occur, due to the inhibiting effect of the trifluoromethyl group on the activity of the hydrogens. Simons and Rambler[14] report the bromination of benzotrifluoride to m-bromobenzotrifluoride at 56° C in the presence of an Fe catalyst, although they state that the reaction was started only after the addition of a considerable amount of catalyst. Also, Kohl[15] has reported vapor phase bromination to mono- and dibromo derivatives by passing bromine and benzotrifluoride through reactors at 700° - 900° C.

Carbon disulfide is commonly employed as a solvent for bromine; so no reaction would be expected at ordinary temperatures between these two liquids. A survey of the literature revealed very little, concerning study of this system. Gerstl[16] stated in 1870, however, reporting the work of Bolas and Groves, that no reaction takes place between bromine and carbon disulfide when the two are heated to 180° C.

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[13]E. T. McBee et al, Ind. Eng. Chem., 39, 420 (1947).

[14]J. H. Simons and E. O. Rambler, J. Am. Chem. Soc., 65, 391 (1943)

[15]C. F. Kohl, Jr., U. S. 2,494,817, Jan. 17, 1950, abstracted in C. A., 44, 4029b (1950).

[16]R. Gerstl, Ber., 3, 508 (1870).

CHAPTER III

EXPERIMENTAL

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A. Apparatus

1. Equilibrium Still

The equilibrium still used to obtain the vapor-liquid equilibrium data was constructed completely of glass according to the specification of a similar still whose construction and operation is described by Jones, Schoenborn, and Colburn.[1] It is composed of a residue chamber, a condensate chamber, and a flash boiler.

Certain modifications were made on the still, which are essentially those described by Kruger.[2] The residue chamber was covered, except for a small window with a layer of asbestos paste to minimize the effects of drafts. A small coil condenser was connected onto the rest and from this was connected a dry ice trap. A further modification was made to Kruger's still in that the system did not open to the atmosphere, but by means of a two-way stopcock could be connected either to an aspirator or to a constant pressure control.

The constant pressure control was used solely for the purpose of maintaining the pressure at 760 mm, at which all runs were made. It consisted of a large (approximately 25 liters) leak-proof metal tank, equipped with a 1/6 HP compressor, connected by rubber tubing to a glass

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[1]C. A. Jones, E. M. Schoenborn, and A. P. Colburn, *Ind. Eng. Chem.*, 35, 666-68 (1943).

[2]J. Kruger, "An Azeotrope in the System Bromine-Carbon Tetrachloride," (Master's thesis, Georgia Institute of Technology, Atlanta, Georgia, 1949), p. 13.

tube, which was in turn connected by means of the two-way stopcock
mentioned above to the still. A mercury manometer was placed in the
system for reading gage pressure. The rubber tubing making the glass
to metal connection was sealed with vacuum wax to both the glass and
metal. Dow-Corning silicone stopcock grease, used on the two-way stop-
cock, was found sufficient to prevent leakage at that point of the
system, the pressure applied being only of the magnitude of 20 mm.

Considerable difficulty was encountered in finding a stopcock
lubricant which would prevent leakage of the liquid mixtures introduced
into the still. It was finally necessary to resort to the use of no-
lub stopcocks, although it was still desirable to use a very thin layer
of Dow-Corning silicone stopcock grease to prevent completely the escape
of bromine vapors into the room. The difficulties encountered led to
the complete removal of the stopcock between the condensate chamber and
the flash boiler described in the Jones-Schoenborn-Colburn still. The
purpose of this stopcock was to prevent a suction effect into the flash
boiler on the withdrawal of samples. No such detrimental effect arose,
however, from its removal, due to the fact that samples taken were
volumetrically quite small.

One final modification involved the addition of a heating coil to
the condensate chamber. This was used only in the study of the system
bromine -- 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane, and its function
will be described in the report on the procedure employed for that
system.

The heating of the residue chamber, the small portion of the still
connecting the residue chamber to the condenser (necessarily maintained

at a higher temperature than the residue chamber to prevent refluxing or fractionation), the flash boiler, and the condensate chamber were all controlled independently by General Radio Co. variacs No. 5, connected to a Sola constant voltage transformer.

A copper-constantan thermocouple, inserted into a thermocouple well in the residue chamber, was used to measure equilibrium temperatures. The cold junction was a bath of finely crushed melting ice. The thermocouple was connected to a Leeds and Northrup No. 7651 potentiometer reading to 0.001 millivolt. The temperature readings were thus accurate to approximately 0.10° C. The thermocouple was calibrated by Kruger.[3] Several checks on boiling points of pure liquids gave satisfactory correlation, so no recalibration was deemed necessary.

2. Fractionating Column (For purification of solvents)

The fractionating column used to purify the 1,1,2-trifluoro-1,2,2-trichloroethane and the carbon disulfide is a five foot glass helix packed column. It was used at a reflux ratio of 20-1.

3. Fractionating Column (For distilling azeotropes)

The smaller fractionating column used for distilling the azeotropes of the systems studied is a total condensation, partial take-off column, packed with 3/16 in. glass helices (packed section: length 40 centimeters, diameter 2 centimeters). The column is equipped with standard taper ground glass joints for distilling flask, thermometer, and take-off. Dow-Corning silicone stopcock grease was used for the thermometer joint

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[3] Ibid., p. 14.

and for the take-off stopcock, although it was found necessary to use a heavier lubricant for the distilling flask joint. A vacuum stopcock grease was used for this. The column when operating was connected to a dry-ice trap which in turn was connected to the constant pressure control apparatus described previously. All runs were made at 760 mm pressure. Ice water was circulated through the condenser. The thermometer used was calibrated in degrees, range -10° - 110° C. Good correlation was observed between the thermometer and thermocouple measurements.

B. Materials

1. Bromine

Merck analyzed C. P. Bromine was used for all systems. No further purification was performed.

2. Solvents

a. 1,1,2-trifluoro-1,2,2-trichloroethane

This solvent, "Freon 113", was obtained from Kinetics Chemicals, Inc. Purification was performed by distillation through the column described previously. A middle cut was taken, boiling point range 46.6° - 46.8° C at 739.6 mm pressure. The boiling point observed at 760 mm agreed with that recorded in the literature (boiling point at 760 mm 47.7° C[4]).

b. 1,1,1,2-tetrachloro-2,2-difluoroethane

This compound, "Genetron 131", was obtained from the General Chemical Division of the Allied Chemical and Dye Corporation as a solid

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[4]E. G. Locke, W. R. Brode, and A. L. Henne, _J. Am. Chem. Soc._, 56, 1727 (1934).

(melting point 40.6° C[5]). No further purification was performed due to the fact that a limited quantity was available. The contributors described the chemical as quite pure. At 760 mm pressure the boiling point observed was in good agreement with that recorded in the literature (boiling point at 760 mm 91.5° C[5]).

c. 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane

This solvent was obtained from Halogen Chemicals Inc., purity listed as 95-98%. The chemical was procured in insufficient quantity to permit further purification. The impurities were thus tolerated, since it was felt that they were probably of similar type chemical constitution. The observed boiling point at 760 mm was 72.5° C; that recorded in the literature is 72° C (no pressure listed).[6]

d. Benzotrifluoride

This solvent was obtained from the Hooker Electrochemical Company, who listed purity as 98% (ASTM). Due to its availability in small quantity no further purification was performed. Observed boiling point at 760 mm was 103.9° C; that recorded in the literature is 103.5° C.[7]

e. Carbon disulfide

Commercial carbon disulfide was purified by the method of

[5]Loc. cit.

[6]A. L. Henne, A. M. Whaley, and J. K. Stevenson, J. Am. Chem. Soc., 63, 3479 (1941).

[7]F. Swarts, Bull. Acad. roy. Belgique [3], 35, 375-420 (1898), abstracted in Chem. Centr., 69[2], 26-27 (1898).

Chenevier.[8] It was allowed to stand overnight with 0.5 cc of bromine per liter. The bromine was then removed by shaking with aqueous potassium hydroxide solution until no color remained in the carbon disulfide layer. This was followed by drying overnight over calcium chloride. Finally, the dried carbon disulfide was fractionated in the column previously described, a center cut boiling point range 45.2 - 45.4° C at 740 mm being retained.

The purified carbon disulfide was placed in a tightly stoppered (ground glass) bottle and stored with the exclusion of light until the investigation of this system was undertaken. A period of about six months intervened. At this time the following tests were run to ascertain that the chemical had not become contaminated during this period:

(1) Refractive Index: Observed at 18° C — 1.6295
                      Recorded (18° C) — 1.62950[9]

(2) Boiling Point: Observed at 760 mm — 46.3° C
                   Recorded (760 mm) — 46.25° C[10]

(3) Methods of testing for C. P. grade carbon disulfide:
    All tests for impurities negative[11]

C. Procedure and Results

   1. System: Bromine — 1,1,2-trifluoro-1,2,2-trichloroethane

      a. Operation of Equilibrium Still

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[8]A. Weissberger and E. Proskauer, Organic Solvents, (London: Oxford University Press, 1935), p. 170.

[9]International Critical Tables, (New York: McGraw-Hill Book Company, 1930), VII, 34.

[10]Ibid., (1928), III, 231.

[11]B. L. Murray, Standards and Tests for Reagent and C. P. Chemicals, Second Edition, (New York: D. Van Nostrand Company, 1927), pp. 192-94.

Solutions ranging in composition from 0% to 100% bromine were introduced into the still by suction from the aspirator. A total of approximately 25 ml of solution was required for the residue and condensate chambers, which were filled separately from a 25 ml Erlenmeyer flask fitted with a standard taper female ground glass joint. A long tube extended from each side of the still. When the Erlenmeyer flask was in position these tubes reached almost to the bottom of the flask; so that very nearly all of the contents could be introduced into the apparatus. The usual procedure for all the systems studied was to start with the pure solvent and make a series of runs, gradually increasing the bromine content.

After the apparatus had been filled, the external pressure of 760 mm was applied. It was necessary to read barometric pressure immediately preceding the start of each run and to set the gage pressure in the tank accordingly. Both barometric and gage pressures were checked several times during each run, and the gage pressure of the tank changed if necessary. Very little difficulty was encountered here, however, since due to the large size of the tank, the air reservoir absorbed almost completely fluctuations in pressure caused by temperature changes. The runs were generally of only one- to two-hour duration.

Once the still has been charged and the pressure of one atmosphere applied, it was necessary to regulate the heat supplied to the flash boiler, the residue chamber, and the portion of the still between the residue chamber and the condenser (Ice water was circulated through both condensers.). This regulation was extremely sensitive. If too little heat was supplied to the residue chamber, operation would cease, while

if too much was supplied, liquid would begin to collect in the flash boiler. Only enough heat was supplied to the flash boiler to vaporize the entering liquid, since superheating was undesirable. Regulation was made so that a few drops of liquid, but no more, could be seen at all times in the flash boiler. The regulation of heat supplied to the small portion of the still between the residue chamber and the condenser was not too sensitive, since it was required only that the temperature be higher than that in the residue chamber.

Equilibrium could generally be quite easily discerned, first by continued proper operation and second by the constancy of temperature for a reasonable period of time (15 to 20 minutes). Once it was certain that equilibration was complete, the equilibrium temperature was read from the thermocouple measurement and samples were withdrawn and analyzed.

The sampling procedure consisted simply of withdrawing the small volume of the liquid in each chamber which might have remained stagnant during the run, and then withdrawing a few drops (generally of weight 0.5 to 2.0 grams depending upon bromine content) into previously weighed weighing bottles containing concentrated potassium iodide solutions. The bottles were immediately reweighed to determine the weight of sample withdrawn, and analyzed by titration of the liberated iodine with approximately 0.2 N standardized sodium thiosulfate solution to a starch indicator end point. Three samples were analyzed for both the liquid and the condensed vapor phases. Agreement was generally quite good. 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. These solutions were standardized by titration against 0.2000 N potassium dichromate solution, prepared by direct weighing. Practically no change occurred in the standard of the sodium thiosulfate solutions in the time required for their consumption, as verified by checks. Starch solution was freshly prepared about every second day.

After each run the contents of the still were completely withdrawn. More of one of the components was then added, and the solution mixed thoroughly. The still could then be recharged, and another run made. Overnight the still was always dried out by passing through it air from a sulfuric acid -- soda-lime drying train. Due to the high volatility of the components, the adhering liquids could be easily removed by the dry air.

The vapor-liquid equilibrium data obtained for this system from the equilibrium still are given in Table I.

b. Results from Fractionating Column

With the data obtained from the equilibrium still it was possible to extrapolate to the approximate azeotropic composition. A mixture of very nearly this composition was volumetrically prepared and fractionated in the small fractionating column previously described, the process being carried out under a pressure of 760 mm. The fractionating power of the column was admittedly low; but since the composition of the charge was almost that of the azeotrope, very little fractionation was required. The still was allowed to operate for a short time under total reflux until the temperature was stabilized, and then samples were withdrawn from the take-off and analyzed. The first liquid which collected

in the take-off tube was withdrawn and discarded, however, to insure

that the analyses were made on the freshly condensed vapor. The azeo-

tropic temperature was recorded.

The azeotrope was found to boil at $41.0°$ C. Analysis showed

45.5 mol % bromine.

c. Test for Possibility of Reaction

Although there seemed to be only a very small possibility

that a reaction had occurred between the components of the system, a

test was performed to determine whether any evidence of the formation

of a new product could be found by refractive index measurements. The

index of refraction of the solvent was measured at $35.0°$ C. A small

amount of bromine was added to make a solution of approximately 10% by

weight. The bromine was then distilled off at the azeotropic composition

in the smaller fractionating column. When no more bromine remained in

the column, which could easily be discerned, both by the disappearance

of color and the exhibition by the liquid coming off, of the boiling

point of the solvent, the distillation was stopped and the refractive

index of the liquid remaining in the still pot determined. The second

measurement checked with the first as far as the accuracy of the

refractometer measurements would allow (five significant figures). Data

for this determination are recorded in Table VI.

d. Volume Change of Mixing

As a final determination for the system, a measurement was

made on the volume change occurring on mixing the two liquids. The extent

to which the actual volume of a mixture of two liquids differs from the

ideal volume gives a very good indication of the non-ideality of the solution. This measurement involved merely the direct determination of the volume resulting upon the mixing of approximately equal measured volumes of the two components. Care was taken to avoid any mechanical loss on mixing. As was to be expected, a large cooling effect was noted upon mixing; so time was allowed for the mixture to equilibrate at room temperature before the final volume measurement was taken. The per cent increase in volume on mixing for this system was found to be 6.2%. The data for this determination are recorded in Table VII. The per cent increase is reported to two figures, although due to the approximate nature of the measurement, the second figure is considered not necessarily significant.

2. System: Bromine — 1,1,1,2-tetrachloro-2,2-difluoroethane

The investigation of this system was conducted in precisely the same manner as that for the preceding system, except for the following modifications, which were necessary due to the fact that the solvent is a low melting solid rather than a liquid at room temperature:

(1) Water at room temperature, rather than ice water, was circulated through the condensers of the equilibrium still for runs made on charges of low bromine content, to prevent solidification of the vapor phase in the condenser.

(2) It was not possible to measure the boiling point (760 mm) of the pure solvent in the equilibrium still. This measurement was made by boiling the solvent in a small distilling flask, whose outlet was connected to the constant pressure control. The temperature was read directly using an Anschütz thermometer, range 40° - 100° C.

(3) In titrating the samples, one further difficulty arose. Upon withdrawing the sample into aqueous potassium iodide solution, the solvent immediately solidified, some of the liberated iodine adhering to this solid mass. It was necessary, therefore, toward the end of each titration to heat the sample above 40.6° C, the melting point of the solvent, in order that all the iodine would pass into solution as I_3^- and allow the completion of the titration.

The system forms an azeotrope of composition 90.8 mol % bromine and boiling at 57.8° C at 760 mm. No evidence of reaction between the components was observed. Complete data from the investigation are recorded in Tables II, VI, and VII.

3. System: Bromine — 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane

Due to the fact that bromine and this solvent are not completely miscible, certain modifications in the procedure for investigation became necessary.

a. Operation of Equilibrium Still

The procedure for the operation of the equilibrium still was precisely the same as that for the study of System No. 1 for all runs made on charges of low bromine content. After a certain concentration of bromine was reached, it was observed that a much larger head was necessary in the condensate chamber for continuous operation. Furthermore, the condensed vapor phase analysis gave an unreasonably high bromine concentration. The difficulty was found to be caused by the separation of the condensed vapor phase into two liquid layers.

It became necessary then to modify the method of analysis for

the condensed vapor phase on runs of high bromine content, although the
original method was still applicable in the single phase region. This
new method of analysis required first the determination of the equilib-
rium concentration of the two liquid layers at an easily reproduced
temperature. This was done at 0° C as will be explained below. Once
this information was available, the analysis could be made in the
following manner. After equilibration was complete and samples taken
from the residue chamber, the entire condensed vapor phase was withdrawn
into a previously weighed bottle, having a ground glass stopper. The
tightly stoppered bottle was immediately reweighed to determine the
weight of both liquid layers, and then its contents transferred to a
separatory funnel immersed in a bath of finely crushed melting ice. The
solution was allowed to stand at 0° C for about forty minutes, during
which time it was felt that equilibration would occur; then the phases
were separated and each weighed. In order to separate the layers it
was necessary to remove the separatory funnel from its bath and shine
a strong light through the solution to see the liquid-liquid interface.
All this could be accomplished in about thirty seconds, however; so it
was felt that no appreciable error was introduced by the warming of the
solution in that short period.

Having determined the weight of each liquid layer and knowing its
composition, it was then an easy matter to calculate the overall composi-
tion of the vapor phase. The accuracy of the method is certainly less
than that of the first method of analysis. Mechanical losses in handling
were unavoidable. A good estimate of error could be made by comparing
the weight of the completely withdrawn vapor phase and the sum of the

two liquid layers, determined after equilibration at 0° C, the loss being of the order of one gram in thirty or roughly 3%. Calculation of the composition was made on the basis of the layers weighed separately, since it was felt that the mechanical loss would be distributed between both layers and thus this method of computation would tend to lessen the error.

Complete vapor-liquid equilibrium data are given in Table III.

b. Results from Fractionating Column

Two runs were made on the fractionating column, approaching the two-phase azeotropic composition from both the high bromine and low bromine sides. The approximate azeotropic composition was determined by extrapolation of data obtained from the equilibrium still and solutions of nearly this composition were volumetrically prepared in each case. The runs were made just as previously described, although two liquid phases were present in the distilling flask at all times. Results from both runs were in good agreement, and the average value was taken as the azeotropic composition. The two-phase azeotrope boiled at 49.1° C; azeotropic composition was 69.5 mol % bromine.

c. Liquid Phase Analyses

The equilibrium compositions of the two liquid layers present below the azeotropic boiling point were determined in order that the complete phase diagram between 0° C and the boiling point of the solvent could be constructed. A quantity (about 25 ml) of the solution in the two liquid phase region was placed in a water bath and allowed to equilibrate at various temperatures between 0.0° C and the azeotropic boiling

point. The solution was allowed to stand with frequent agitation in the bath for about one hour (temperature regulation ± 0.1° C). At the end of this period samples were pipetted from each layer into previously weighed weighing bottles containing concentrated potassium iodide solution and analyses were made in the usual manner. A strong light was shined through the solution in order that the liquid-liquid interface could be easily distinguished. Great care was taken in withdrawing samples in order that each sample should contain liquid from one layer only. The data obtained from these determinations are recorded in Table IV.

Although these analyses were carried out at normal atmospheric pressure, which averaged perhaps 20 mm less than one atmosphere, it was felt that the effect of this pressure difference on the results obtained was totally negligible.

d. Test for Possibility of Reaction

This test was performed in exactly the same manner as that for System No. 1. The data are given in Table VI.

e. Volume Change of Mixing

The procedure was the same as that for System No. 1, except that due to the limited solubility it was impossible to prepare a single phased equi-volume mixture. The per cent volume increase for a six to one (solvent to bromine) volumetric solution was approximately 2%. Complete data are given in Table VII.

4. System: Bromine - Benzotrifluoride

All procedures used for this investigation were precisely the same as those used for study of System No. 1. An azeotrope was found to

exist - boiling point at 760 mm 58.1° C, composition 96.7 mol % bromine.
No evidence of reaction between the components was observed. Complete
data on this system are given in Tables V, VI, and VII.

5. System: Bromine - Carbon Disulfide

The study on this system was started using the same procedures
followed in the study of System No. 1. Several runs were made in the
equilibrium still on charges of low bromine content, preliminary data
indicating that no azeotrope existed in the system. When runs were
attempted with charges of higher bromine content, a definite reaction
was observed to take place in the still. A high boiling residue collected
in the lower end of the flash boiler and a solid material in very small
quantity could be seen in the samples after titration. Furthermore, no
satisfactory end point could be obtained in titrating the samples.
Study on this system was, thus, discontinued. No attempt was made to
identify the products of reaction.

CHAPTER IV

DISCUSSION OF RESULTS

CHAPTER IV

DISCUSSION OF RESULTS

1. System: Bromine -- 1,1,2-trifluoro-1,2,2-trichloroethane

Plots of the vapor-liquid equilibrium data are given in Figures 1 and 2. Figure 1 is a plot of equilibrium temperature _vs._ mol fraction bromine, the lower curve being liquid phase concentration and the upper curve vapor phase concentration. The azeotrope is seen to boil at 41.0° C at 760 mm pressure, a boiling point depression of 6.6° C. This large depression is consistent with the large internal pressure difference (3170 atms) between the components and with the high per cent volume increase observed on mixing equal volumes of the two liquids (6.2%). Figure 2 is a plot of mol fraction bromine in the vapor _vs._ mol fraction bromine in the liquid, the curve crossing the 45° line at 0.455 mol fraction bromine, the azeotropic composition.

The likelihood of reaction between the components, as discussed in Chapter II, seemed very small. The test performed in determining the refractive index of the solvent before and after refluxing with bromine rather conclusively verified this assumption.

2. System: Bromine -- 1,1,1,2-tetrachloro-2,2-difluoroethane

Figures 3 and 4 are plots of the vapor-liquid equilibrium data for this system, corresponding respectively to Figures 1 and 2 for System No. 1. The minimum boiling point, that of the azeotrope at 760 mm, is seen to be 57.8° C, a depression of 1.1° C. This boiling point depression is large considering the great difference in boiling points of the constituents, again showing consistency with internal pressure

difference (2960 atms) and per cent volume increase on mixing (4.7%).
The curve in Figure 4 is seen to cut the 45° line at the azeotropic
composition, 0.908 mol fraction bromine.

The possibility of a reaction between the components of the
system was fairly conclusively ruled out by the test performed. This
was expected to be the case.

3. System: Bromine -- 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane

In Figures 5 and 6 are plotted the vapor-liquid and liquid-
liquid equilibrium data obtained from the investigation of this system.
Figure 5 is the complete phase diagram of the system above 0° C, showing
the boiling point of the two-phase azeotrope to be 49.1° C and its
composition 0.695 mol fraction bromine. The large boiling point depres-
sion exhibited and the fact that the two liquids are only partially
miscible is indicative of the large deviation from ideality of the
solution. This is consistent with the large internal pressure difference
between the two liquids (3340 atms), the greatest of any of the systems
investigated. In regard to the volume change of mixing, it is not fair
to make a comparison between the proportionally small per cent increase
observed for this system (2%) with that observed in the other systems
studied, since due to the limited miscibility of the components it was
possible to prepare a mixture of only relatively low bromine content
and still retain a single liquid phase.

Figure 6 is a plot of mol fraction bromine in the vapor vs. mol
fraction bromine in the liquid, analogous for this type of system to
Figure 2 for System No. 1. The curve is seen to cut the 45° line at
the azeotropic composition.

As discussed in Chapter II, the possibility of reaction between the components of the system seems highly unlikely. The results of the test for evidence of reaction carried out were not absolutely conclusive, since a change was noted in the fifth significant figure of the measured refractive indices. This slight deviation is not attributed, however, to a reaction between the components of the system, in view of their very nature. The change may perhaps be ascribed to the presence of a small amount of low boiling impurity in the solvent. In any event the change of the refractive index measurement in the last figure is not felt to be of significance.

4. System: Bromine - Benzotrifluoride

Figures 7 and 8 are plots of the vapor-liquid equilibrium data for this system, corresponding respectively to Figures 1 and 2 for System No. 1. From these two plots the azeotrope is seen to have a composition of 0.967 mol fraction bromine and a boiling point at 760 mm of 58.1° C. The boiling point depression, 0.8° C, is considerable in view of the great difference in boiling points of the constituents; however this, as in the case of the other systems, is consistent with the large difference in internal pressures of the two liquids (2740 atms). In addition to this, the per cent volume increase observed in mixing (4.4%) indicates the high deviation from ideality of the solution.

The chance of a reaction's occurring between the components of this system seemed greater than in the other systems investigated, due to the presence of hydrogen atoms on the benzene ring of the benzo-trifluoride. However, as mentioned in Chapter II, the presence of the trifluoromethyl group on the ring considerably lessened the possibility

of a reaction in the absence of a catalyst. The test performed in determining the refractive indices of the solvent before and after contact with bromine appears to verify this conclusion.

5. System: Bromine - Carbon Disulfide

No definite conclusions can be drawn from the investigation made upon this system due to the reaction that occurred during its course. The preliminary data obtained, showed no indication of the system's exhibiting azeotropic phenomena. Despite the fact that the boiling points of the liquids are not far apart, in view of the relatively small internal pressure difference between the components (1030 atms) this is not surprising. It must be reiterated, however, that no definite conclusions could be drawn from this study concerning the vapor-liquid equilibria for the system.

The reaction observed was surprising considering that no mention of the occurrence of such a reaction was found in the literature. It is, of course, within the realm of possibility that the reaction was caused by the presence of some impurity in the solvent, although this seems unlikely in view of the fact that standard tests made for the presence of any impurities in appreciable quantities were all negative. It is not possible with the information at hand to make any statement concerning the nature of the reaction, since no investigation of this matter was pursued.

In general, the experimentally obtained results from all the systems studied, with the exception of System No. 5, are in accord with what might have been predicted from a consideration of the properties of these systems. A comparison of the phase diagrams of the various

systems shows that the boiling point depressions of the azeotropes formed were in at least semi-quantitative agreement with the extent of deviation from ideal behavior, as estimated from internal pressure differences and per cent volume increases observed on mixing. The results thus appear to be consistent with the accepted theories concerning azeotropic phenomena.

CHAPTER V

SUMMARY

CHAPTER V

SUMMARY

1. Constant pressure vapor-liquid equilibria studies were carried out for five systems involving bromine and bromine solvents.

2. Results of these investigations were as follows:

    a. System: Bromine -- 1,1,2-trifluoro-1,2,2-trichloroethane

       Azeotrope formed: Boiling point (760 mm), 41.0° C

                  Composition, 0.455 mol fraction bromine

    b. System: Bromine -- 1,1,1,2-tetrachloro-2,2-difluoroethane

       Azeotrope formed: Boiling point (760 mm), 57.8° C

                  Composition, 0.908 mol fraction bromine

    c. System: Bromine -- 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane

       Two-phase azeotrope formed: Boiling point (760 mm), 49.1° C

                  Composition, 0.695 mol fraction bromine

    d. System: Bromine -- Benzotrifluoride

       Azeotrope formed: Boiling point (760 mm), 58.1° C

                  Composition, 0.967 mol fraction bromine

    e. System: Bromine -- Carbon disulfide

       Investigation discontinued due to occurrence of reaction

3. Liquid-liquid equilibrium measurements were made for the system bromine -- 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane, the constituents being only partially miscible.

4. Measurements were made to determine the per cent volume change

occurring on mixing the two liquids of each system. Positive deviation from Raoult's law was indicated in all cases in which azeotrope formation was exhibited.

5. Tests involving refractive index determinations conducted upon all the systems except that of bromine and carbon disulfide, ascertained that no reaction had taken place between the constituents.

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BIBLIOGRAPHY

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APPENDIX I

TABLES AND FIGURES

TABLE I: Vapor-Liquid Equilibria Data for System Bromine --
1,1,2-trifluoro-1,2,2-trichloroethane

Temperature °C	Mol Fraction Bromine in Vapor	Mol Fraction Bromine in Liquid
47.6	0.000	0.000
45.7	0.105	0.049
44.2	0.197	0.103
43.4	0.248	0.132
42.5	0.307	0.200
41.0	0.455	0.455
41.2	0.523	0.669
42.0	0.551	0.839
43.4	0.590	0.889
46.1	0.630	0.919
51.6	0.791	0.973
58.9	1.000	1.000

TABLE II: Vapor-Liquid Equilibria Data for System Bromine —
1,1,1,2-tetrachloro-2,2-difluoroethane

Temperature °C	Mol Fraction Bromine in Vapor	Mol Fraction Bromine in Liquid
91.6	0.000	0.000
89.0	0.149	0.027
77.6	0.461	0.138
71.0	0.600	0.238
64.8	0.726	0.389
61.5	0.778	0.508
57.9	0.889	0.872
57.8	0.908	0.908
57.9	0.925	0.935
58.4	0.981	0.991
58.9	1.000	1.000

TABLE III: Vapor-Liquid Equilibria Data for System Bromine --
1,1,1,3,3-pentafluoro-2,2,3-trichloropropane

Temperature °C	Mol Fraction Bromine in Vapor	Mol Fraction Bromine in Liquid
72.5	0.000	0.000
66.6	0.217	0.049
62.7	0.342	0.087
59.5	0.434	0.126
58.1	0.443	0.146
51.0	----	0.375
49.1	0.695	----
53.0	0.71[a]	0.961
55.7	0.80[a]	0.978
56.5	0.81[a]	0.981
56.8	----	0.985
57.6	----	0.995
58.9	1.000	1.000

[a]Analyses performed gravimetrically (see page 25).

TABLE IV: Liquid-Liquid Equilibria Data for System Bromine —
1,1,1,3,3-pentafluoro-2,2,3-trichloropropane

Temperature °C	Mol Fraction Bromine in Upper Layer	Mol Fraction Bromine in Lower Layer
0.0	0.270	0.974
20.3	0.354	0.971
35.3	0.434	0.954
40.1	0.468	0.942
45.4	0.504	0.935
48.0	0.529	0.926

TABLE V: Vapor-Liquid Equilibria Data for System Bromine --
Benzotrifluoride

Temperature °C	Mol Fraction Bromine in Vapor	Mol Fraction Bromine in Liquid
103.9	0.000	0.000
96.5	0.249	0.040
90.2	0.386	0.080
80.1	0.578	0.175
71.1	0.736	0.298
61.0	0.865	0.630
58.4	0.942	0.934
58.1	0.967	0.967
58.5	0.978	0.988
58.9	1.000	1.000

TABLE VI: Data on Tests for Evidence of Reaction

Solvent	Temperature of Measurements °C	Refractive Index before Contact with Bromine	Refractive Index after Contact with Bromine
$CF_2ClCFCl_2$	35.0	1.3512	1.3512
CCl_3CClF_2	45.0	1.4032	1.4032
$CF_3CCl_2CF_2Cl$	35.0	1.3453	1.3458
$C_6H_5CF_3$	35.0	1.4073	1.4073

TABLE VII: Data on Volume Changes Observed on Mixing

Temperature °C	Solvent	Vol. of Bromine mls	Vol. of Solvent mls	Ideal Vol. of Mixture mls	Actual Vol. of Mixture mls	% Vol. Increase
30	$CF_2ClCFCl_2$[a]	1.52	1.70	3.22	3.42	6.2
44.5	CCl_3CClF_2[a]	3.20	3.87	7.07	7.40	4.7
28	$CF_3CCl_2CF_2Cl$	0.50	3.00	3.50	3.57	2.0
23	$C_6H_5CF_3$[a]	2.00	2.10	4.10	4.28	4.4

[a]Considerable cooling noted on mixing with bromine.

TABLE VIII: Data on Physical Properties of Systems Investigated

Component	B. P. Obs. at 760 mm	Diff. in B. P.'s of Br_2 and Solvent	Density (t°C)	Molar Volume at t°C	Internal Pressure Estimate	Diff. in Estimated Internal Pressure of Br_2 and Solvent
	°C	°C	gms/ml	mls	atms	atms
Br_2	58.9	---	3.1023 (25)[a]	51.52	5390	---
$CF_2ClCFCl_2$	47.6	11.3	1.56354 (25)[b]	119.9	2220	3170
CCl_3CClF_2	91.6	32.7	1.598 (41)[c]	127.6	2430	2960
$CF_3CCl_2CF_2Cl$	72.5	13.6	1.6681 (20)[d]	142.3	2050	3340
$C_6H_5CF_3$	103.9	45.0	1.19632 (14)[e]	122.1	2650	2740
CS_2	46.3	12.6	1.2554 (25)[f]	60.64	4360	1030

[a]International Critical Tables, (New York: McGraw-Hill Book Company, 1928), III, 20.

[b]E. G. Locke, W. R. Brode, and A. L. Henne, J. Am. Chem. Soc., 56, 1727 (1934).

[c]Determined experimentally.

[d]A. L. Henne, A. M. Whaley, and J. K. Stevenson, J. Am. Chem. Soc., 63, 3479 (1941).

[e]Chem. Centr., 69², 26-27 (1898), citing F. Swarts, Bull. Acad. roy. Belgique [3], 35, 375-420 (1898).

[f]International Critical Tables, op. cit., p. 23.
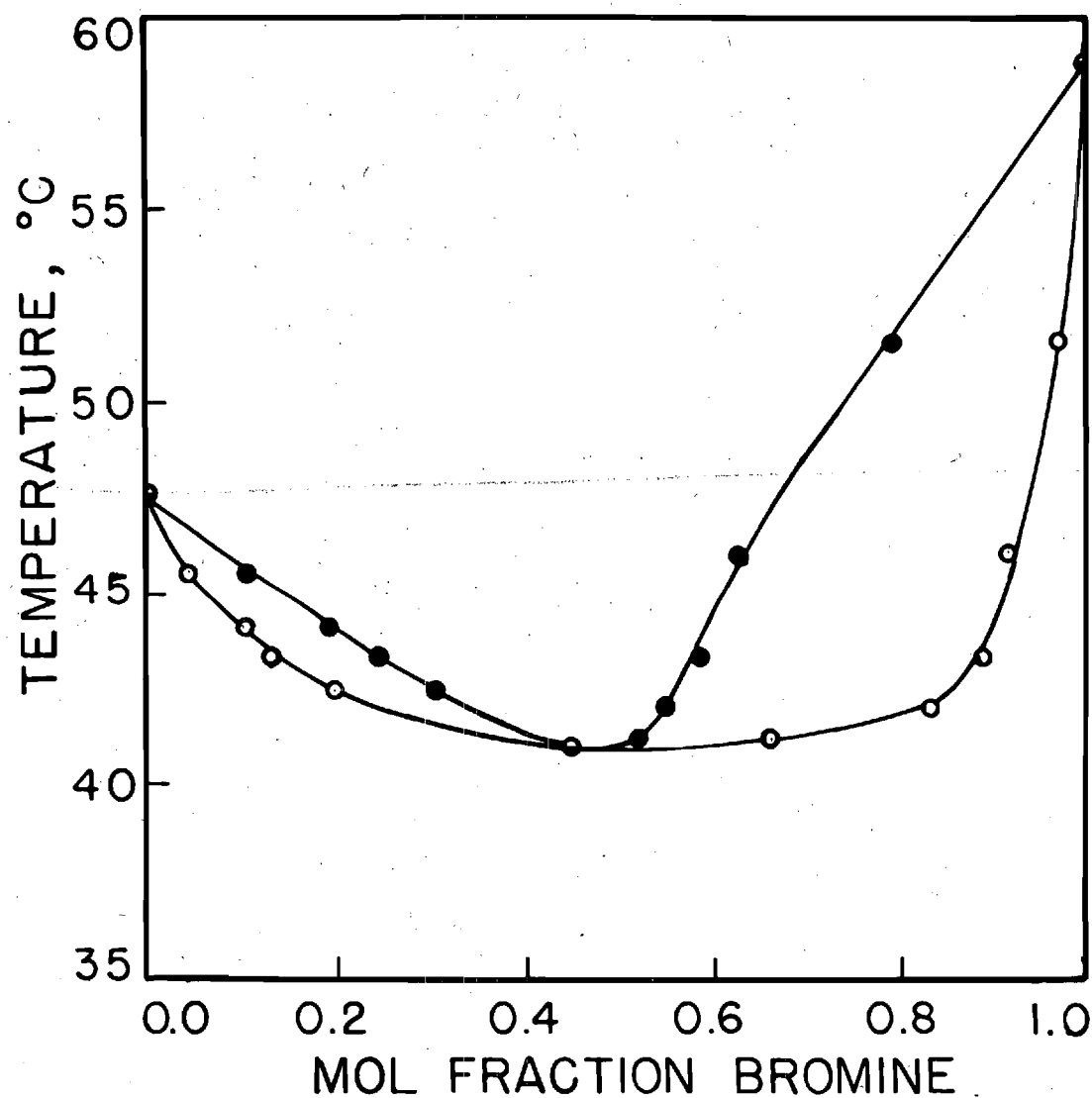
FIGURE I

TEMPERATURE−COMPOSITION DIAGRAM
FOR SYSTEM $Br_2 - CF_2ClCFCl_2$ AT 760 mm
PRESSURE: ● ,VAPOR; ○ , LIQUID,
◐ ,VAPOR AND LIQUID
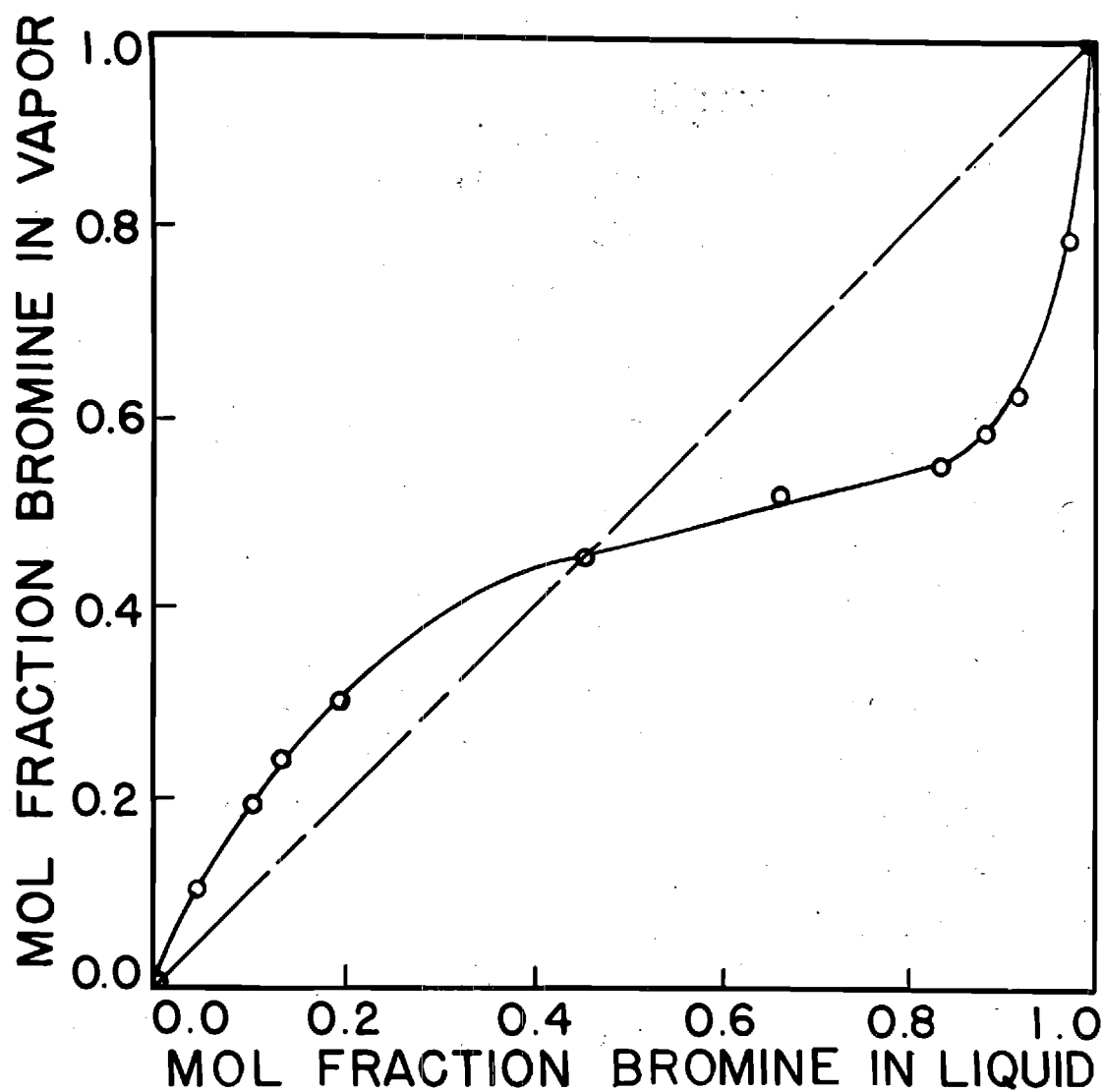
FIGURE 2

VAPOR–LIQUID EQUILIBRIUM DIAGRAM
FOR SYSTEM Br_2–$CF_2ClCFCl_2$ AT 760mm
PRESSURE
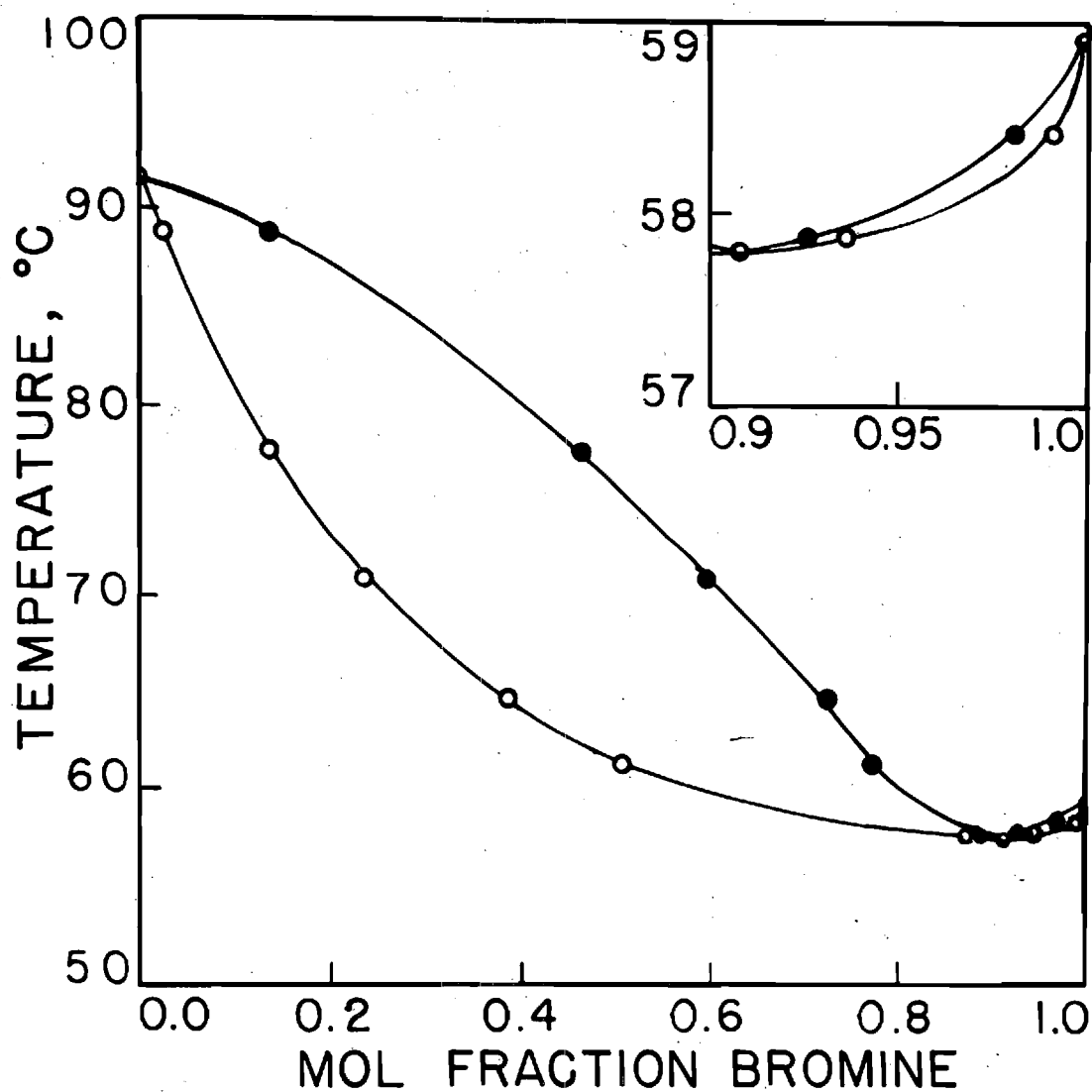
FIGURE 3

TEMPERATURE—COMPOSITION DIAGRAM
FOR SYSTEM $Br_2-CCl_3CClF_2$ AT 760mm
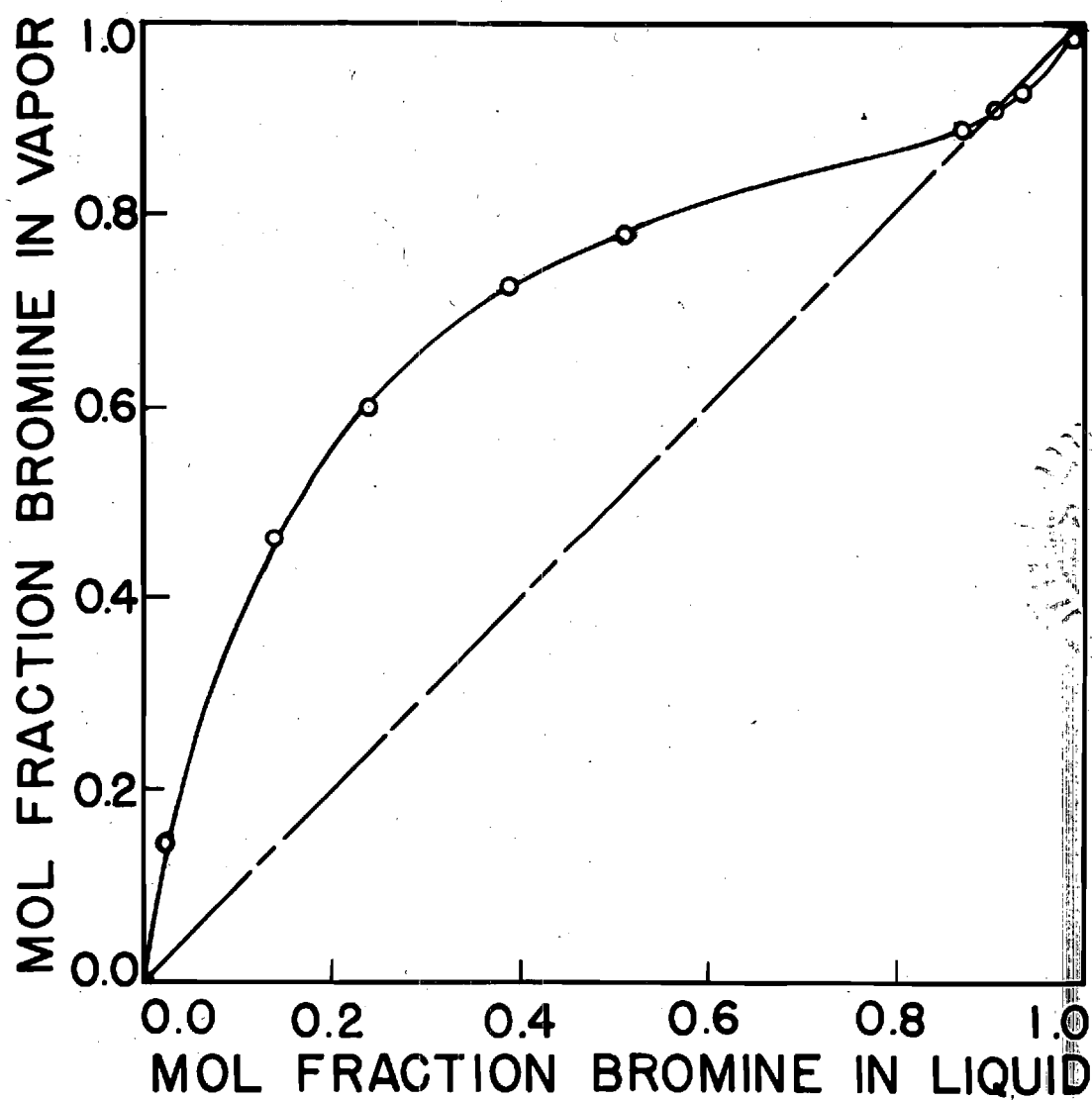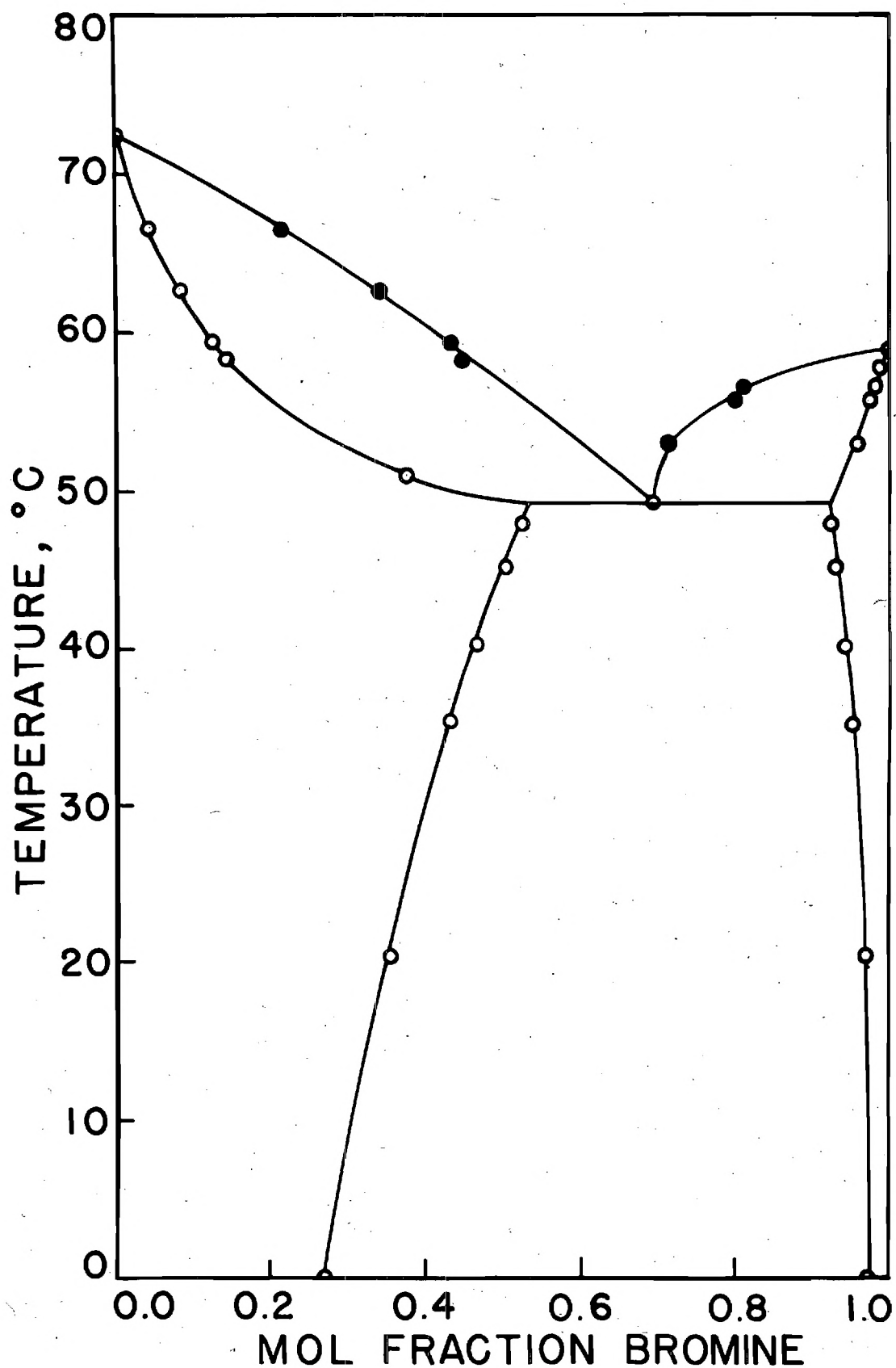PRESSURE: •, VAPOR; ○, LIQUID;
◉, VAPOR AND LIQUID

FIGURE 4

VAPOR–LIQUID EQUILIBRIUM DIAGRAM
FOR SYSTEM Br$_2$–CCl$_3$CClF$_2$ AT 760 mm
PRESSURE

FIGURE 5

TEMPERATURE-COMPOSITION DIAGRAM FOR
SYSTEM $Br_2-CF_3CCl_2CF_2Cl$ AT 760mm PRESSURE
● ,VAPOR; ○ ,LIQUID; ◒ ,VAPOR AND LIQUID
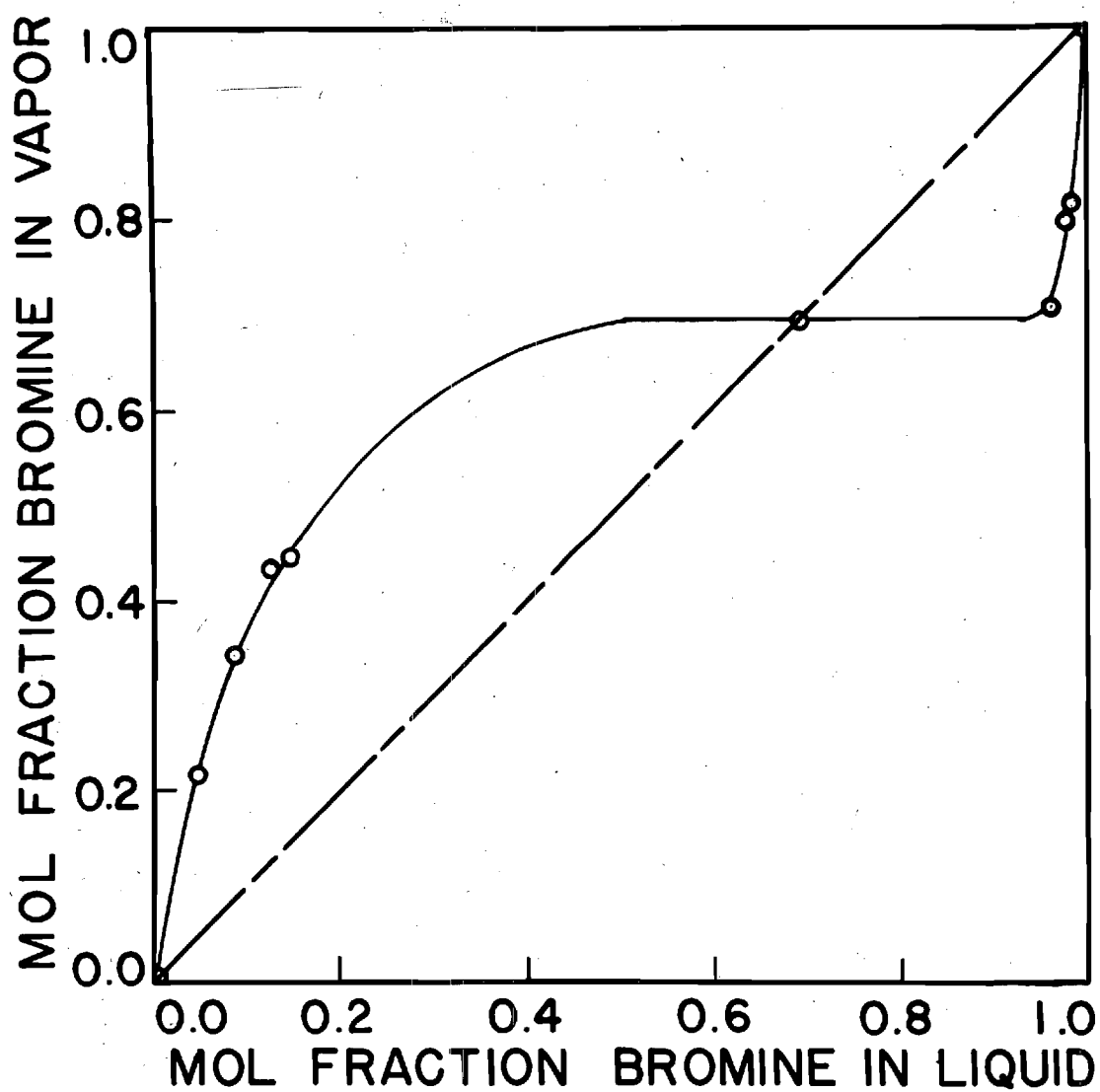
FIGURE 6

VAPOR-LIQUID EQUILIBRIUM DIAGRAM
FOR SYSTEM $Br_2 - CF_3 CCl_2 CF_2 Cl$ AT
760 mm PRESSURE
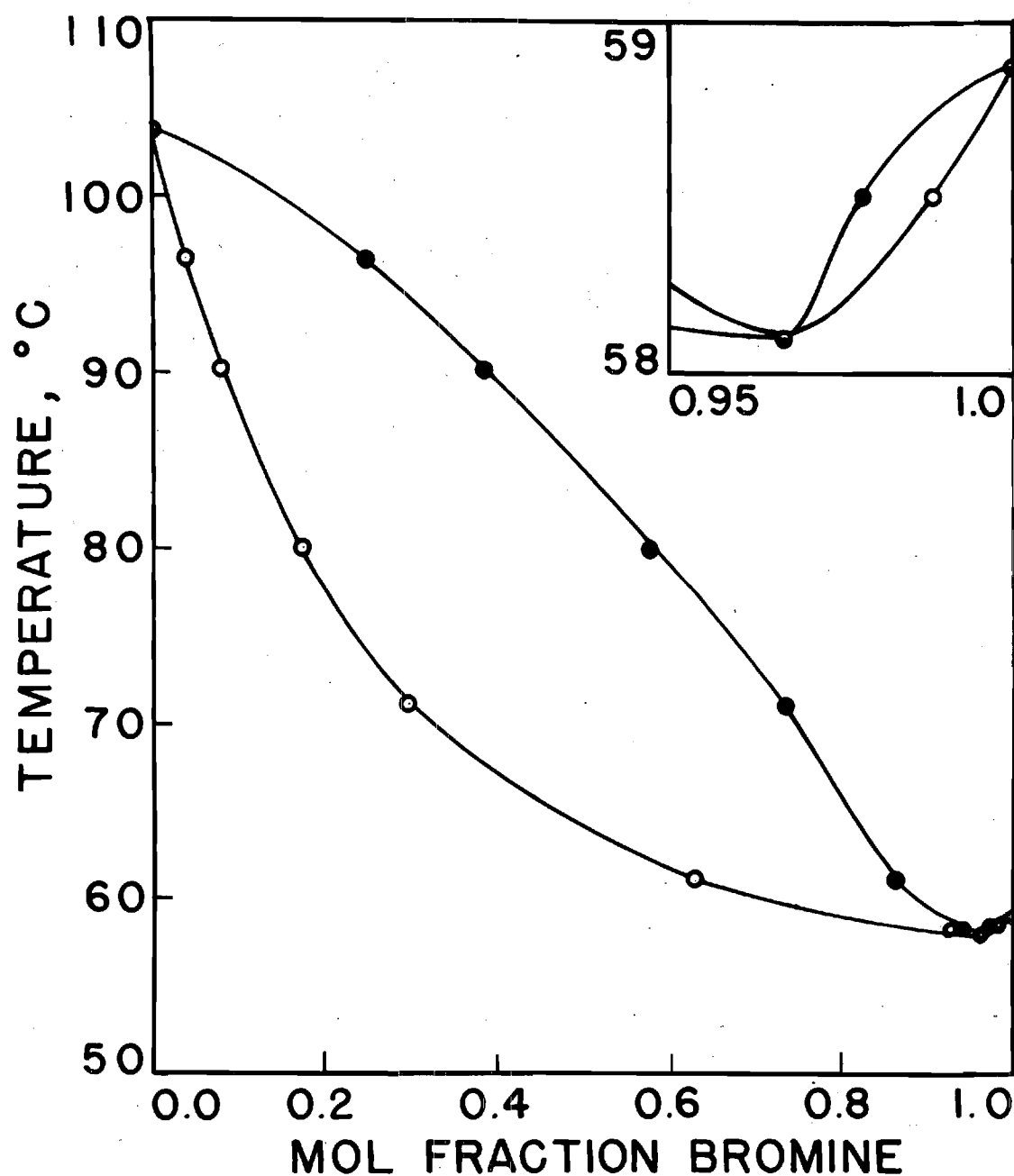
FIGURE 7

TEMPERATURE—COMPOSITION DIAGRAM
FOR SYSTEM $Br_2-C_6H_5CF_3$ AT 760 mm
PRESSURE: ● , VAPOR; ○ , LIQUID;
◐ , VAPOR AND LIQUID
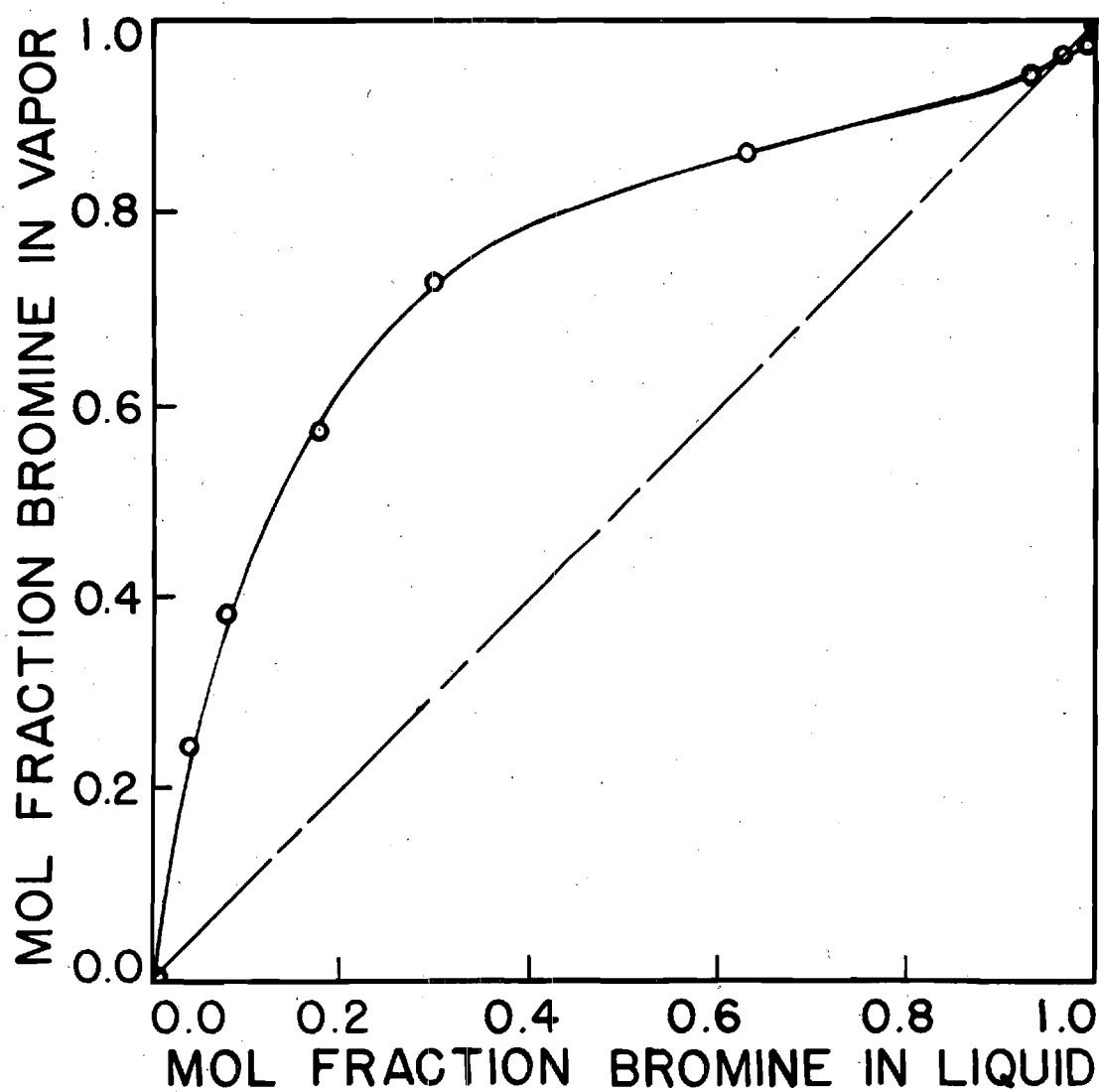
FIGURE 8

VAPOR–LIQUID EQUILIBRIUM DIAGRAM FOR SYSTEM $Br_2-C_6H_5CF_3$ AT 760mm PRESSURE

APPENDIX II

SAMPLE CALCULATIONS

APPENDIX II

SAMPLE CALCULATIONS

1. The calculation involved in the analytical procedure for determining bromine concentration in single phases is illustrated below:

Data

Weight of weighing bottle and KI solution —   71.3030 gms

Weight of weighing bottle and KI solution + sample — 71.9766 gms

Weight of sample —   0.6736 gms

Milliliters of 0.2068 N $Na_2S_2O_3$ standard solution — 16.37   mls

Calculation

Reactions involved: $3I^- + Br_2 = 2 Br^- + I_3^-$

$$I_3^- + 2 S_2O_3^= = 3 I^- + S_4O_6^=$$

Thus: Equivalent weight of bromine = Equivalent weight of iodine

Equivalent weight of iodine = Gram-atomic weight of iodine

Equivalent weight of bromine = Gram-atomic weight of bromine

Equivalent weights of bromine = Normality of $Na_2S_2O_3$ solution

$$x \frac{Milliliters\ of\ Na_2S_2O_3}{1000}$$

$$= \frac{0.2068 \times 16.37}{1000} = 0.003385$$

Mols of bromine = 1/2 x Equivalent weights of bromine

$$= 1/2 \times 0.003385 = 0.001693$$

Weight of bromine = Equivalent weights of bromine x Equivalent weight of bromine

$$= 0.003385 \times 79.92 = 0.2705\ gms$$

Weight of CCl_3CClF_2 = Weight of sample - Weight of bromine

$$= 0.6736 - 0.2705 = 0.4031 \text{ gms}$$

Mols of CCl_3CClF_2 = $\dfrac{\text{Weight of } CCl_3CClF_2}{\text{Molecular weight of } CCl_3CClF_2}$

$$= \frac{0.4031}{203.86} = 0.001977$$

Total mols = Mols of bromine + Moles of CCl_3CClF_2

$$= 0.001693 + 0.001977 = 0.003670$$

Mol fraction bromine = $\dfrac{\text{Mols of bromine}}{\text{Total mols}}$

$$= \frac{0.001693}{0.003670} = 0.461$$

2. The calculation involved in the analytical procedure for determining overall bromine concentration in condensed vapor phases containing two liquid layers is illustrated below:

Data

Equilibrium bromine concentration at 0.0° C in the two-phase liquid mixture of bromine and $CF_3CCl_2CF_2Cl$:

Upper layer: Weight fraction bromine   =   0.200

Lower layer: Weight fraction bromine   =   0.960

Weight upper layer -- 9.862 gms

Weight lower layer -- 22.758 gms

Total weight sample -- 32.620 gms

Calculation

Weight bromine in upper layer   =   Weight upper layer x Weight fraction bromine

$$= 9.862 \times 0.200 = 1.972 \text{ gms}$$

Weight bromine in lower layer = Weight lower layer x Weight fraction

bromine

= 22.758 x 0.960 = 21.848 gms

Total weight bromine = Weight bromine in upper layer + Weight bromine

in lower layer

= 1.972 + 21.848 = 23.820 gms

Total weight $CF_3CCl_2CF_2Cl$ = Total weight sample - Total weight bromine

= 32.620 - 23.820 = 8.800 gms

$$Mols\ bromine\ =\ \frac{Total\ weight\ bromine}{Molecular\ weight\ bromine}$$

$$=\ \frac{23.820}{159.84}\ =\ 0.1490$$

$$Mols\ CF_3CCl_2CF_2Cl\ =\ \frac{Total\ weight\ CF_3CCl_2CF_2Cl}{Molecular\ weight\ CF_3CCl_2CF_2Cl}$$

$$=\ \frac{8.800}{237.41}\ =\ 0.0371$$

Total mols = Mols bromine + Mols $CF_3CCl_2CF_2Cl$

= 0.1490 + 0.0371 = 0.1861

$$Mol\ fraction\ bromine\ =\ \frac{Mols\ bromine}{Total\ mols}$$

$$=\ \frac{0.1490}{0.1861}\ =\ 0.800$$

3. The calculation involved in determining the per cent volume increase

occurring on mixing liquids is illustrated below:

Data

Volume bromine added --- 2.00 mls.

Volume benzotrifluoride added --- 2.10 mls

Actual volume of mixture --- 4.28 mls

Calculation

Ideal volume of mixture = Volume bromine added + Volume benzo-
trifluoride added

$$= 2.00 + 2.10 = 4.10 \text{ mls}$$

Volume increase = Actual volume of mixture - Ideal volume of mixture

$$= 4.28 - 4.10 = 0.18 \text{ ml}$$

Per cent volume increase $= \dfrac{\text{Volume increase}}{\text{Ideal volume of mixture}} \times 100\%$

$$= \dfrac{0.18}{4.10} \times 100\% = 4.4\%$$

4. The calculation involved in estimating the internal pressures of
the liquids studied is illustrated below:

Data

Liquid --- $CF_2ClCFCl_2$

Boiling point at 760 mm --- 47.6° C

Density at 25° C --- 1.564 gms/ml

Calculation (See page 7.)

Energy of vaporization $= \Delta E_v \doteq 5280 + (24.5 \times$ atmospheric boiling
point in °C)

$$\doteq 5280 + (24.5 \times 47.6) = 6450 \text{ cal}$$

Molar volume at 25° C $= V = \dfrac{\text{Molecular weight}}{\text{Density at 25° C}}$

$$= \dfrac{187.40}{1.564} = 119.9 \text{ mls}$$

Internal pressure $= \dfrac{\Delta E_V}{V}$

$= \dfrac{6450}{119.9} = 53.9 \; \text{cal/ml} = 2220 \; \text{atm}$