

AN AZEOTROPE IN THE SYSTEM  
BROMINE-CARBON TETRACHLORIDE

*crossed*

A THESIS

Presented to  
the Faculty of the Division of Graduate Studies  
Georgia Institute of Technology

In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science in Chemistry

by

Jerome Kruger

September 1949

AN AZEOTROPE IN THE SYSTEM  
BROMINE-CARBON TETRACHLORIDE

Approved:

*[Signature]*  
\_\_\_\_\_

*[Signature]*  
\_\_\_\_\_

*[Signature]*  
\_\_\_\_\_

*[Signature]*  
\_\_\_\_\_

Date Approved by Chairman Sept. 7, 1949

#### ACKNOWLEDGMENTS

This is to thank Dr. W. M. Spicer who suggested this problem and who was a constant source of aid and advice throughout the entire investigation.

## TABLE OF CONTENTS

	PAGE
Approval Sheet. . . . .	ii
Acknowledgements. . . . .	iii
Chapter I, Introduction . . . . .	1
Chapter II, Theoretical Discussion. . . . .	3
1. Ideal Solutions. . . . .	3
2. Non-Ideal Solutions. . . . .	4
3. Azeotropes . . . . .	9
4. Application of Concepts to System Bromine- Carbon Tetrachloride . . . . .	11
Chapter III, Experimental . . . . .	13
A. Apparatus. . . . .	13
1. Equilibrium Still . . . . .	13
2. Fractionating Column. . . . .	14
B. Materials. . . . .	14
C. Procedure and Results. . . . .	15
1. Operation of Equilibrium Still. . . . .	15
2. Results from Fractionating Column . . . . .	18
Chapter IV, Discussion of Results . . . . .	21
Chapter V, Summary. . . . .	24
BIBLIOGRAPHY. . . . .	25
APPENDIX I, TABLE AND FIGURES . . . . .	27
APPENDIX II, SAMPLE CALCULATION . . . . .	31

## CHAPTER I

### INTRODUC TION

AN AZEOTROPE IN THE SYSTEM  
BROMINE-CARBON TETRACHLORIDE

CHAPTER I

INTRODUCTION

In attempting to develop methods whereby azeotropic mixtures can be separated, it is convenient to have as a research tool a constant boiling mixture that contains one colored component so that the extent of separation can be ascertained merely by inspection. This investigation resulted from the need for such an azeotrope for thermal diffusion studies. Naturally, an azeotrope of bromine because of its intense color was thought of as a suitable possibility. An extensive search through the literature, however, revealed no such azeotrope.

Lewis and Storch<sup>1</sup> found that solutions of bromine and carbon tetrachloride show a large positive deviation from Raoult's law indicating, as it shall be shown in Chapter II, that an azeotrope may exist in this system since the boiling points of the components are not far apart. Since bromine vapor and liquid are highly colored and carbon tetrachloride is colorless, this system was selected as a probable one in which to find a colored azeotrope.

This investigation consists of the following:

1. The discovery and proof of an azeotrope in the system bromine-

---

<sup>1</sup>G. N. Lewis and H. Storch, J. Am. Chem. Soc. 39, 2544 (1917).

carbon tetrachloride and the determination of its composition and boiling point at a specific barometric pressure.

2. A study of the vapor-liquid equilibrium of the system bromine-carbon tetrachloride.

3. A determination of the effect on the volume of the azeotrope mixture because of deviations from Raoult's Law.

## CHAPTER II

### THEORETICAL DISCUSSION



## CHAPTER II

## THEORETICAL DISCUSSION

1. Ideal Solutions

Glasstone<sup>1</sup> defines an ideal solution as "one which obeys Raoult's law over the whole range of composition at all temperatures and pressures." This law discovered empirically by Raoult in 1887 states that the partial pressure,  $p_i$ , of any constituent in a liquid solution is equal to the product of its mole fraction,  $N_i$ , and its vapor pressure,  $p_i^\circ$ , in the pure state; or expressed mathematically,

$$p_i = N_i p_i^\circ. \quad (1)$$

This idealized form can be made exact for non-ideal gases by replacing the partial pressures by fugacities so that Equation (1) becomes

$$f_i = N_i f_i^\circ \quad (2)$$

where  $f_i$  is the fugacity of component i in the vapor or in the liquid in equilibrium with it and  $f_i^\circ$  is the fugacity of the pure component.

As a consequence of Raoult's law in the form of Equation (2) two facts present themselves; namely, that there is no heat change when two liquids are mixed and, likewise, there is no volume change. This is so because Raoult's law implies that each of the components acts independently

---

<sup>1</sup>S. Glasstone, Thermodynamics for Chemists, (New York: D. Van Nostrand Company, 1947), p. 317.

of the other, there being no alteration of the field of force surrounding the dissimilar molecules which would cause an attraction or repulsion.

This indicates that only those systems whose constituents are similar as to intermolecular forces and possess nearly equal molal volumes will obey Raoult's law. Hildebrand<sup>2</sup> has, however, pointed out that, with respect to the equal size requirement, a much more significant criterion for adherence to Raoult's law than equal molal volumes is nearly equal molecular radii, since the molal volumes of two molecules may differ considerably and yet the molecular radii may be nearly equal thus not greatly altering the structure of the solution and causing deviations from Raoult's law.

A further basis for ideality was pointed out by Hildebrand<sup>3</sup> who proved thermodynamically that only those liquids which have identical values of  $(\frac{\partial P}{\partial T})_V$  can obey Raoult's law at all temperatures and pressures.

## 2. Non-Ideal Solutions

If the requirements of nearly equal molecular size and similarity of intermolecular forces are not met for each of the pure components making up a liquid solution, deviation from Raoult's law results and the solution is designated as non-ideal.

There are two ways in which deviations from Raoult's law (Equation (2)) can occur, e.g., positive and negative deviations. Of the two the positive is the more frequently observed in nature.

---

<sup>2</sup>J. H. Hildebrand, Chem. Rev., 44, 37 (1949).

<sup>3</sup>J. H. Hildebrand, Solubility of Non-Electrolytes, Second Edition, (New York: Reinhold Publishing Corporation, 1936), p. 64.

When a system exhibits positive deviations, the ratio,  $f_1/f_1^0$ , is greater than its mole fraction  $N_1$ . For the negative case the ratio,  $f_1/f_1^0$ , is less than  $N_1$ .

As a result of these definitions, the manifestations of positive and negative deviations were stated as follows by Hildebrand<sup>4</sup>:

"1) A positive deviation from Raoult's law is generally accompanied by an absorption of heat when the pure liquids are mixed, and a negative deviation is generally accompanied by an evolution of heat upon mixing two pure liquids.

"2) Positive deviations from Raoult's law are usually accompanied by an expansion in volume when pure liquids are mixed while negative deviations are accompanied by a contraction."

It now remains to be considered what the causes of these deviations are. In general, these deviations can be attributed to three different phenomena acting in a solution which give rise to intermolecular forces. These are (1) polarity, (2) solvation and association (chemical forces), and (3) van der Waals forces.<sup>5</sup>

The intermolecular forces due to polarity may be divided into those between permanent dipoles and those between a permanent dipole and an induced dipole. This case will not be considered further since it does not apply to the system under investigation. This is so, because, as Hildebrand<sup>6</sup> has pointed out, the simplest indication of polarity is furnished by a high dielectric constant. Bromine and carbon tetrachloride

---

<sup>4</sup>Ibid., pp. 57 and 59.

<sup>5</sup>Most authors include the forces due to polarity when they discuss van der Waals forces. In this paper, following the nomenclature of Hildebrand, only dispersion forces will be called van der Waals forces.

<sup>6</sup>J. H. Hildebrand, op. cit., p. 78.

have the low values of  $3.2^7$  and  $2.24^8$  respectively, and both exhibit zero dipole moment. Consequently, polarity is not a significant factor in this case.

Likewise, the forces which arise from the second phenomenon play a very small role in the present investigation. These forces may be divided into the following classes: (1) the coulombic force between charged molecules and ions; (2) the valence force leading to electron exchange at small distances in the formation of covalent bonds and thus of new molecular species; and (3) hydrogen bonding.

Because of the similarity of the electron systems of bromine and carbon tetrachloride and the lack of a possibility of hydrogen bonding chemical intermolecular forces are of little effect. It may be pointed out, however, that there does exist a slight possibility that a substitution reaction somewhat like



may occur. This appears highly unlikely in the temperature range (50 to  $80^\circ \text{C.}$ ) at which this process was carried out and without the presence of a catalyst, because of the higher electronegativity of the chlorine with respect to the bromine. At higher temperatures it has been shown by Willard<sup>9</sup> that a reaction does take place. He found, however, that no reaction occurred under  $100^\circ \text{C.}$  Experimental evidence that no reaction

---

<sup>7</sup>International Critical Tables, Vol. VI, (New York: McGraw-Hill Book Company, 1929), p. 75.

<sup>8</sup>Ibid., p. 83.

<sup>9</sup>J. E. Willard, University of Wisconsin, Private Communication.

occurred will be cited later (p. 19).

The third factor, van der Waals forces, is the most important one in a system of non-polar molecules.<sup>10</sup> When two molecules, like or unlike, approach one another there is a tendency for their rapidly moving electron systems to interact, due to their tendency to move in phase with each other. The forces that result from these interactions are van der Waals forces or, more accurately, dispersion forces, the type of van der Waals force which exists in non-polar systems. This amounts to a system of rapidly rotating dipoles of variable polarizability and momentum.

In general, the interaction results in both attractive and repulsive potentials. Lennard-Jones<sup>11</sup> gives the following expression which combines both potentials, the first term being the repulsive potential and the second the attractive:

$$= j/r^{12} - k/r^6 \quad (3)$$

where  $j$  and  $k$  are constants called interaction constants and  $r$  is the distance between molecules. In the interior of the liquid there results a balance between the attractive and repulsive forces which gives rise to what is called the internal pressure.<sup>12</sup> This is frequently defined as the quantity  $(\frac{\partial E}{\partial V})_T$ . Since  $(\frac{\partial E}{\partial V})_T$  is equal to the change in internal energy resulting from an increase in volume at a constant temperature,

---

<sup>10</sup>J. H. Hildebrand, op. cit., p. 93.

<sup>11</sup>J. E. Lennard-Jones, Z. phys. chem. B 11, 222 (1930).

<sup>12</sup>S. Glasstone, Textbook of Physical Chemistry, Second Edition, (New York: D. Van Nostrand Company, 1946), p. 479.

it may be looked upon as a measure of the work done in overcoming the internal pressure during a volume change in a liquid.

It can be seen from the thermodynamic equation of state,

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P, \quad (4)$$

that if the external pressure,  $P$ , is neglected since it is very small compared to the internal pressure, the latter can be represented by

$$P_i = T\left(\frac{\partial P}{\partial T}\right)_V. \quad (5)$$

Finally, another expression for  $P_i$  can be obtained from the van der Waals equation,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (6)$$

By differentiating this equation with respect to temperature at constant volume one obtains

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} \quad (7)$$

which when multiplied by  $T$  gives

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V - b} = P + \frac{a}{V^2}. \quad (8)$$

It follows, therefore, from the definition of the internal pressure,  $P_i$ , and Equations (4) and (8) that

$$P_i = \frac{a}{V^2}. \quad (9)$$

This is not strictly correct because it is based upon the inexact van der Waals equation.

It was stated on page 4 that only those liquids which have identical values of  $(\frac{\partial P}{\partial T})_V$  can obey Raoult's law at all temperatures and pressures. Since  $T(\frac{\partial P}{\partial T})_V$  is approximately equal to the internal pressure, it follows that the greater the difference in the internal pressure of two liquids the greater the deviation from Raoult's law. Since the internal pressure is a measure of the attractive forces in a liquid, it would seem reasonable to expect that two liquids possessing identical internal pressures would not change the environmental forces of each other, whereas if the internal pressures were different there would be a change and deviations would occur. It is found that these deviations are of a positive nature and that the extent of these deviations are roughly proportional to the difference of the internal pressures of the two components of the solution.<sup>13</sup>

### 3. Azeotropes

When a non-ideal binary solution exhibiting positive deviations contains two liquids that have boiling points that are not too far apart, there results a maximum in the total vapor pressure versus composition curve (or a minimum in the boiling point curve). As a consequence of this maximum in the vapor pressure curve, the mixture possessing the composition represented by this point has a vapor pressure higher (or a boiling point lower) than any other combination of the two components

---

<sup>13</sup>Ibid., p. 677.

or than either of the two pure components. Further, such a mixture, when distilled, does not change in composition, the proportions of the two components being identical in the liquid and vapor phases. Such a mixture is called a constant boiling mixture or an azeotropic mixture (Greek: to boil unchanged).

Ewell, Harrison, and Berg<sup>14</sup> state that the formation of an azeotrope depends on two factors, (1) the magnitude of the deviation from Raoult's law, and (2) the difference in the boiling points of the two pure components. The smaller the deviations from Raoult's law, the smaller the difference between the boiling points must be before an azeotrope will exist. This is because, if the boiling points are widely separated, the vapor pressure of any mixture of the two components will not exceed that of the highest boiling pure component unless the deviations from Raoult's law are quite large.

This indicates another requirement that must be imposed before an azeotrope can be definitely said to exist in a given system. This requirement is that the system must be studied in a small pressure range. If a system is studied at a sufficiently high external pressure, there is a possibility that the difference in the boiling points of the two pure components may increase at different rates with an increase in pressure, and yield a non-azeotropic system. Nutting and Horsely<sup>15</sup> give some instances of a phenomenon of this sort.

---

<sup>14</sup>R. H. Ewell, J. M. Harrison, and L. Berg, Ind. Eng. Chem., 36, 871 (1944).

<sup>15</sup>H. S. Nutting and L. H. Horsely, Anal. Chem., 19, 602 (1947).



#### 4. Application of Concepts to System Bromine-Carbon Tetrachloride

From the above considerations, it is now necessary to show that the system bromine-carbon tetrachloride exhibits deviations from Raoult's law and that the boiling points of the two constituents are close enough together to form a constant boiling mixture.

There are many indications that the system bromine-carbon tetrachloride exhibits positive deviations from Raoult's law. Lewis and Storch<sup>16</sup> showed that just such a situation exists. They found that the ratio of  $p/p^0 = 0.048$  for bromine at  $N = 0.025$  and  $25^{\circ}\text{C}$ . Since  $p/p^0$  is greater than  $N$  and therefore not equal as Raoult's law demands, the system can be said to exhibit a fairly large positive deviation. This is to be expected since the internal pressure difference between carbon tetrachloride and bromine is 2630 atm.<sup>17</sup> Another reason for this system exhibiting a deviation is the large difference in molal volumes of the carbon tetrachloride (97.1 c.c.)<sup>18</sup> and the bromine (51.2 c.c.)<sup>18</sup>. The molecular radii also show a significant difference,  $1.14 \text{ \AA}$ <sup>19</sup> for bromine and  $1.76 \text{ \AA}$ <sup>20</sup> for carbon tetrachloride, this being a better basis for non-ideality (see page 4). Thus both an alteration in intermolecular forces and a difference in size contribute to positive deviations in the system

---

<sup>16</sup>G. N. Lewis and H. Storch, J. Am. Chem. Soc., 39, 2544 (1917).

<sup>17</sup>R. H. Ewell, J. M. Harrison, and L. Berg, op. cit.

<sup>18</sup>J. H. Hildebrand, Solubility of Non-Electrolytes, p. 127.

<sup>19</sup>Linus Pauling, Nature of the Chemical Bond, Second Edition, (Ithaca: Cornell University Press, 1945), p. 165.

<sup>20</sup>L. O. Brockway and F. T. Wall, J. Am. Chem. Soc., 56, 2372 (1934).

bromine-carbon tetrachloride.

It now remains to be seen if the boiling point difference is sufficiently small to yield an azeotrope. There is no definite analytical procedure to determine this. The only approach is to compare the system under consideration with some other azeotropic system which exhibits deviations of equal or less magnitude and a boiling point spread that is equal or greater than it. Such a system is benzene-n-heptane. This system bears a similarity to the one under investigation in that its constituents are non-polar and are incapable of undergoing hydrogen bonding or other types of association. As with bromine-carbon tetrachloride internal pressure is the main criterion for non-ideality.

This system, which has been shown to exhibit a constant boiling mixture,<sup>21</sup> has a boiling point spread of 18.2° C. as compared to 18.0° C. for bromine-carbon tetrachloride and an internal pressure difference of 1132 atm.<sup>22</sup> as compared to 2630 atm. for the latter. Thus, since this system which has a greater boiling point spread and less positive deviation exhibits a constant boiling mixture, it would seem reasonable to expect an azeotrope to exist in the system bromine-carbon tetrachloride.

---

<sup>21</sup>R. F. Marschner and W. P. Cropper, Ind. Eng. Chem., 38, 262 (1946).

<sup>22</sup>J. H. Hildebrand, Solubility of Non-Electrolytes, pp. 104-105.

## CHAPTER III

### EXPERIMENTAL

## CHAPTER III

## EXPERIMENTAL

## A. Apparatus

## 1. Equilibrium Still

An equilibrium still whose design and operation is described by Jones, Schoenborn, and Colburn<sup>1</sup> was constructed to determine liquid-vapor equilibria data. This apparatus is composed of a residue chamber, a condensate chamber and a flash boiler to vaporize the stream returning from the latter to the former. This arrangement insures that a uniform concentration exists in the residue chamber at equilibrium. This still was chosen for this investigation because it is built entirely of glass (a very necessary requirement when bromine is involved); it requires small samples; the time of operation is not excessively long; and it is capable of yielding accurate results.

Certain additions and modifications were made to the still described by Jones et al. The residue chamber was completely covered with a thin layer of asbestos paste except for a small window, provided so that the liquid level could be observed. This was added to minimize the effect of drafts. A small 7.5 cm. long ice water condenser was added to the vent to the surroundings. To this was added a dry ice trap. These two additions were made to prevent any vapors from escaping from the system. The dry ice trap also had as one of its functions the prevention of moisture from entering the system. Dow-Corning silicone stopcock grease was

---

<sup>1</sup>C. A. Jones, E. M. Schoenborn, and A. P. Colburn, Ind. Eng. Chem., 35, 666 (1943).

used on the stopcocks.

The heating of the residue chamber and flash boiler was controlled by General Radio Co. variacs # V-5 connected to a Sola constant voltage transformer so that once adjustment was obtained there was no change.

Equilibrium temperatures were measured by a copper-constantan thermocouple inserted into the thermocouple well of the residue chamber. The cold junction was a bath of fine crushed melting ice. The thermocouple was connected to a Leeds & Northrup # 7651 potentiometer reading to 0.001 millivolts so that the temperature readings were accurate to approximately 0.10 C. The thermocouple was calibrated against a corrected 100° X 0.1° C 76 mm. immersion thermometer. The transition point of sodium sulfate decahydrate was also used in the calibration.<sup>2</sup>

## 2. Fractionating Column

The fractionating column described by Trimble<sup>3</sup> was used to prepare the azeotrope of bromine and to determine its boiling point. This column is a five foot glass helix packed column used at a reflux ratio of 20 - 1. The thermometer used with the column was an Anschütz thermometer covering the range 40° - 100° C. It was calibrated against the thermometer used in the calibration of the thermocouple.

## B. Materials

Bakers' analysed c.p. bromine was used. Merck carbon tetrachloride was purified by washing with sulfuric acid and then distilled water, and

---

<sup>2</sup>W. C. Eichelberger, J. Am. Chem. Soc., 56, 800 (1934).

<sup>3</sup>A. T. Trimble, Master's Thesis, Georgia Institute of Technology, 1949, p. 30.

drying over phosphorous pentoxide overnight. The carbon tetrachloride was then fractionated in the column described above. A center cut of about 80% of the original charge was retained. A boiling point of 76.0° C. (corr.) at 739.1 mm. was exhibited which agrees with the value from the literature calculated at this same pressure. The index of refraction at 25° C was found using an Abbe' refractometer to be 1.4576 as compared to 1.4575 from the literature.<sup>4</sup>

### C. Procedure and Results

#### 1. Operation of Equilibrium Still

Solutions of compositions ranging from 0% to 100% bromine in carbon tetrachloride were introduced into the equilibrium still by suction with an aspirator. A 25 ml. Erlenmeyer flask fitted with a standard taper female joint contained the solution. The tube leading from the condensate chamber was immersed almost to the bottom of the sample flask. When in this position a standard taper joint through which the chamber tube protrudes fits into the joint at top of the flask. When filling the still the flask was placed loosely in this position so that some air could enter to displace the solution entering the still. When the still was filled, the bottle was pushed tightly into position and thus the small amount of bromine solution remaining in the tube could not enter the room. The still was entirely filled through the tube leading from the condensate chamber. When this chamber was full the overflow liquid entered the residue chamber through the flash boiler. About 25 ml. of solu-

---

<sup>4</sup>B. Pesce and Evdorinnoff, Gazzetta Chimica Italiana, 70, 723 (1940).

tion was introduced into the condensate chamber, half of this going to the residue chamber.

After the heating of the still was adjusted so that only one-half of a milliliter or less of liquid was seen boiling in the lower end of the flash boiler, the attainment of equilibrium required from forty minutes to one hour. Great care had to be taken to assure that superheating did not occur. In general when the heating was adjusted as just described, this difficulty was removed. Because of the high volatility of the bromine and carbon tetrachloride, ice water was circulated through the main condenser as well as the small condenser connected to the vent.

When equilibrium was reached, the still was allowed to operate in this state for about ten minutes and the temperature repeatedly checked to make certain that no change occurred. Two milliliters of liquid was withdrawn from each chamber and discarded, since the liquid in the lower part of the chambers was somewhat trapped and had a composition slightly different from the equilibrium value. Samples were then removed from the condensate and residue chambers and introduced directly into previously weighed weighing bottles containing potassium iodide solution. The weighing bottles were then reweighed and the iodine liberated by the bromine titrated with approximately 0.2 N standardized sodium thiosulfate solution using a starch indicator. The analytical procedure is the one described by Scott.<sup>5</sup> The sodium thiosulfate solution and the starch indicator were prepared using the procedure described by Rieman and Neuss.<sup>6</sup>

---

<sup>5</sup>W. W. Scott, Standard Methods of Chemical Analysis, Fifth Edition, Volume I, (New York: D. Van Nostrand Co., 1939), p. 191.

<sup>6</sup>W. Rieman and J. D. Neuss, Quantitative Analysis, (New York: McGraw-Hill Book Company, 1937), pp. 177 and 185.

Attempts were made at the beginning of the investigation to devise a method whereby the bromine could be determined photometrically. These were, however, unsuccessful because the bromine absorbed light so strongly that samples to be analyzed had to be diluted to such an extent that the method became highly inaccurate. Specific gravity and refractive index methods were ruled out because of the extreme corrosiveness and volatility of the solutions handled.

When the analysis was completed the contents of the still were removed and the still dried by drawing air through the outlets of the two chambers until it was dry. This procedure was followed only at the beginning of this investigation as it was found that this method of drying actually introduced water into the system which contaminated the bromine solutions. It was found that the presence of water in these solutions gave low boiling points. This was a source of great difficulty and error. To correct this the still was dried out by drawing air through it which had been dried by passage through concentrated sulfuric acid and soda-lime. The air was drawn through very slowly for a period of about 15 hours. A bromine solution was then introduced and after equilibrium and analysis the solution remaining in the still was not removed. Instead, bromine or carbon tetrachloride was added to the still to bring the volume of its contents up to 25 ml. and to change the composition of the still's charge. A run was then carried out on this solution. In this manner the chance of water entering the system was reduced. About five runs were carried out in this manner before the still was completely emptied and dried as before.

The liquid-vapor equilibrium data obtained by using the equilibrium still



are tabulated in Table I. Since the pressure was not regulated, the atmospheric pressures prevailing at the time each run was made are also recorded.

## 2. Results from Fractionating Column

Solutions having a composition greater than the azeotropic composition determined approximately from the vapor-liquid measurements made on the equilibrium still were fractionated in order to determine accurately the boiling point and composition of the azeotrope.

The boiling point was found to be  $57.7^{\circ}\text{C}$  (corr.) at 735.6 mm. Its composition was found to be 88.8 weight % bromine.

Pure bromine was introduced into the column and was found to boil at  $58.0^{\circ} - 58.1^{\circ}\text{C}$  (corr.), at 736.2 mm., a value which agrees with the one calculated by using the Clausius-Clapeyron equation.

An analysis of the still pot was made. The results are as follows:

Composition Weight % Bromine		
Original Solution	Distillate (Azeotrope)	Still Pot
91.4%	88.8%	94.9%

An experiment was carried out to determine whether reaction had taken place. A bromine-carbon tetrachloride solution containing approximately 11% bromine was fractionated, the bromine, or rather the azeotrope being completely removed until the distillate coming off exhibited the boiling point of carbon tetrachloride. The refractive index of carbon tetrachloride used was determined before making up the solution. When the bromine was completely removed the index of refraction of the carbon tetrachloride remaining in the still pot was determined. The results

were;

$n_{26.50} \text{ CCl}_4$	$n_{26.50} \text{ CCl}_4$
Before fractionating	After fractionating
1.4558	1.4558

thus indicating that no high boiling compound was formed by a reaction between bromine and carbon tetrachloride.

### 3. Volume of Azeotropic Mixture

In order to roughly determine if there is an increase in volume when bromine and carbon tetrachloride are mixed, the volume of a given quantity of the azeotropic mixture was measured and this compared to the volume of the same weight calculated assuming ideality.

About 5 ml. of the azeotropic mixture was introduced into a weighed graduated stoppered glass tube to some arbitrary graduation. The tube was stoppered tightly and weighed. After emptying, cleaning, and drying, distilled water was introduced into this tube up to the same mark where the level of the bromine solution had previously been. The tube and contents were then reweighed. The whole operation was carried out at room temperature which did not vary appreciably in the short time that was required to carry out the experiment. The error involved in the volume measurement was less than  $\pm 0.05$  cc.

Knowing the density of the water at the temperature prevailing, the volume of the water and thus the volume occupied by the azeotropic mixture was determined. The volume of the weighed quantity of the constant boiling mixture measured was then calculated knowing its composition and using densities obtained from the International Critical

Tables<sup>7</sup> assuming ideality. It was found that,

Actual Volume	Ideal Volume
Measured at 29.1° C	at 29.1° C
5.34 cc.	5.24 cc.

Thus it is seen that a volume expansion occurs when bromine and carbon tetrachloride are mixed.

---

<sup>7</sup>International Critical Tables, Volume III, pp. 20 and 28.

## **CHAPTER IV**

### **DISCUSSION OF RESULTS**

## CHAPTER IV

## DISCUSSION OF RESULTS

The results of the liquid-vapor equilibrium measurements are plotted in three different ways in Figures 1, 2, and 3. In Figure 1, a plot is made of the equilibrium boiling points versus the composition of the liquid for the lower curve and the composition of the vapor in equilibrium with the liquid on the upper curve. This boiling point curve shows a definite minimum at approximately 57.8° C at a composition of 0.89 mole fraction bromine. Figure 2 is a plot of mole fraction of bromine in the vapor versus mole fraction of bromine in the vapor. The curve cuts the dashed 45° line at a composition very near the composition of the azeotropic mixture found by fractionation. Figure 3 is a plot of relative volatility versus the mole fraction of bromine in the liquid. The relative volatility is defined by the expression,

$$\alpha = \frac{Y_a X_b}{Y_b X_a} \quad (1)$$

where  $\alpha$  is the relative volatility,  $X_a$  and  $Y_a$  are the mole fractions of the more volatile component in the liquid and vapor respectively, and  $X_b$  and  $Y_b$  are those for the other component. The relative volatilities are tabulated in Table I also. It will be noted from Figure 3 that the concentration of the bromine in the liquid at the point where  $\alpha = 1$ , is the same as that found from the other methods. According to Griswold and Ludwig<sup>1</sup> the smoothness of the relative volatility curve is a rather

---

<sup>1</sup>J. Griswold and E. E. Ludwig, Ind. Eng. Chem., **35**, 117 (1943).

sensitive test for the consistency of the data. The one point that is off appears to be off in Figures 1 and 2, also. On the whole, the vapor-liquid equilibrium data appear to be consistent.

The fact that the pressure was not regulated is not of great significance. This can be seen by making a rough calculation using the approximate form of the Clausius-Clapeyron equation

$$\frac{\Delta T}{\Delta P} = \frac{RT^2}{\Delta H_v P} \quad (2)$$

If boiling point of carbon tetrachloride is substituted for  $T$  since it was the highest temperature attained, the mean value of the molar heats of vaporization of bromine and carbon tetrachloride is substituted for  $\Delta H_v$ , and  $P$  is replaced by the pressure in the middle of the range observed,  $\Delta T / \Delta P$  is found to be approximately  $0.05^\circ \text{C./mm.}$  The error due to pressure changes in the range in which the measurements were made, 734-741 mm., is less than this value since the temperature used in this calculation was the largest measured.

The facts that a minimum exists in the boiling point curve and that a fraction was obtained in the fractionation boiling lower than pure bromine and having essentially the same boiling point and composition as the minimum of the boiling point curve, are indicative that an azeotrope does indeed exist in this system. Also the fact that the percentage of bromine increased over that before fractionation was carried out is a further proof that an azeotrope is present in the system. This is so because if no azeotrope existed, the lowest boiling component, bromine, would be removed first and its percentage would decrease in the still pot.

Since the opposite happened (page 18) either an azeotrope exists in the system or reaction has taken place.

The possibility that reaction did take place was ruled out by the experiment (p. 19) in which the refractive index of the carbon tetrachloride before and after fractionation was determined and showed no change. Had a reaction taken place the index of refraction would have changed because of the new products formed. It is unlikely that all of these products would have been removed by fractionation before the refractive index of the carbon tetrachloride in the still pot was determined because the boiling points of some of these bromine substituted products would be higher than carbon tetrachloride because of their higher molecular weights.

The volume determination is further evidence that a positive deviation from Raoult's law does occur.

This investigation can be extended and made more accurate by obtaining the equilibrium data at a controlled constant pressure. Isothermal measurement would also be of interest. Other systems such as those involving bromine as one component and using as a second component various low boiling fluorocarbons or silicon tetrachloride would merit study.

## **CHAPTER V**

### **SUMMARY**



## **BIBLIOGRAPHY**

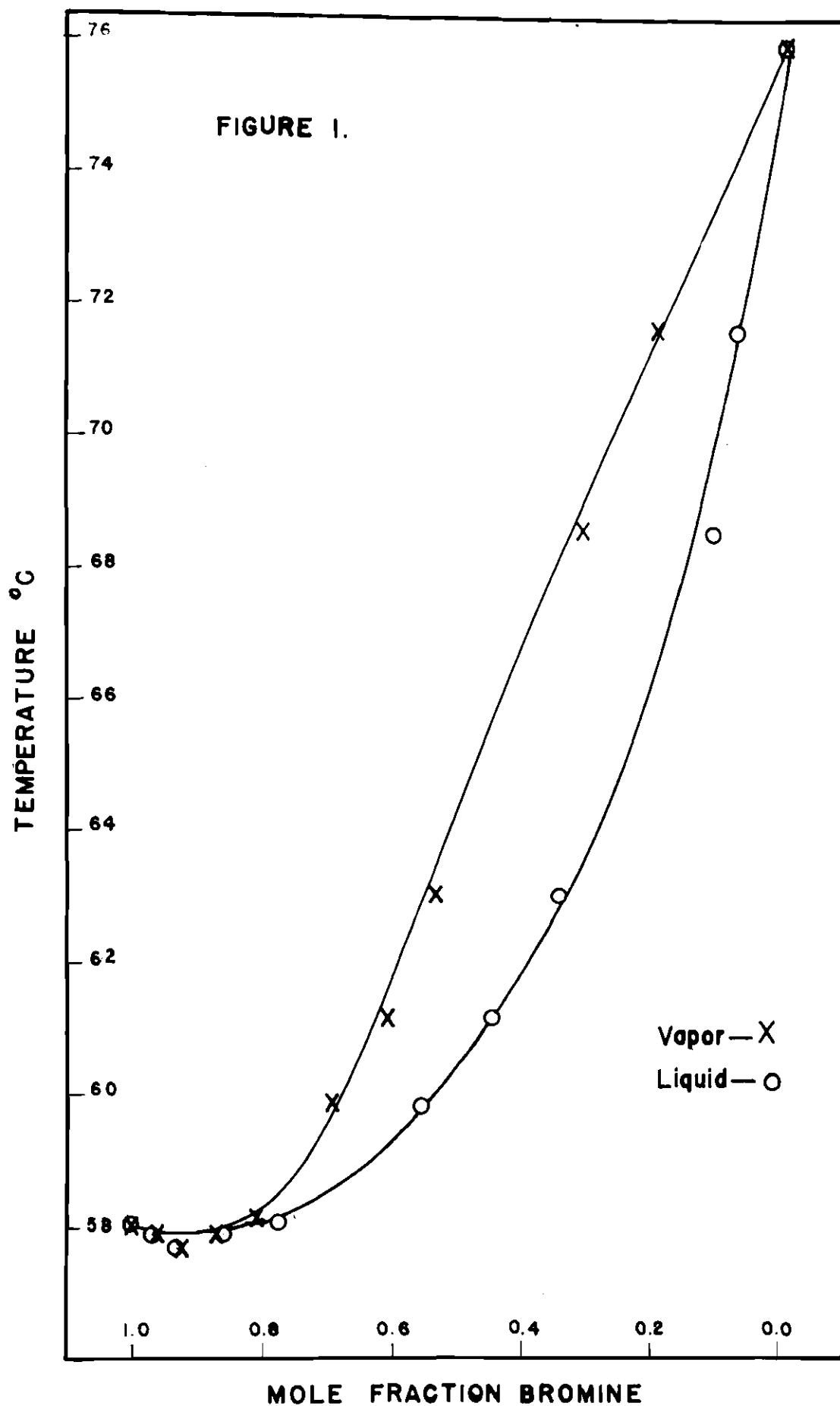
## APPENDIX I

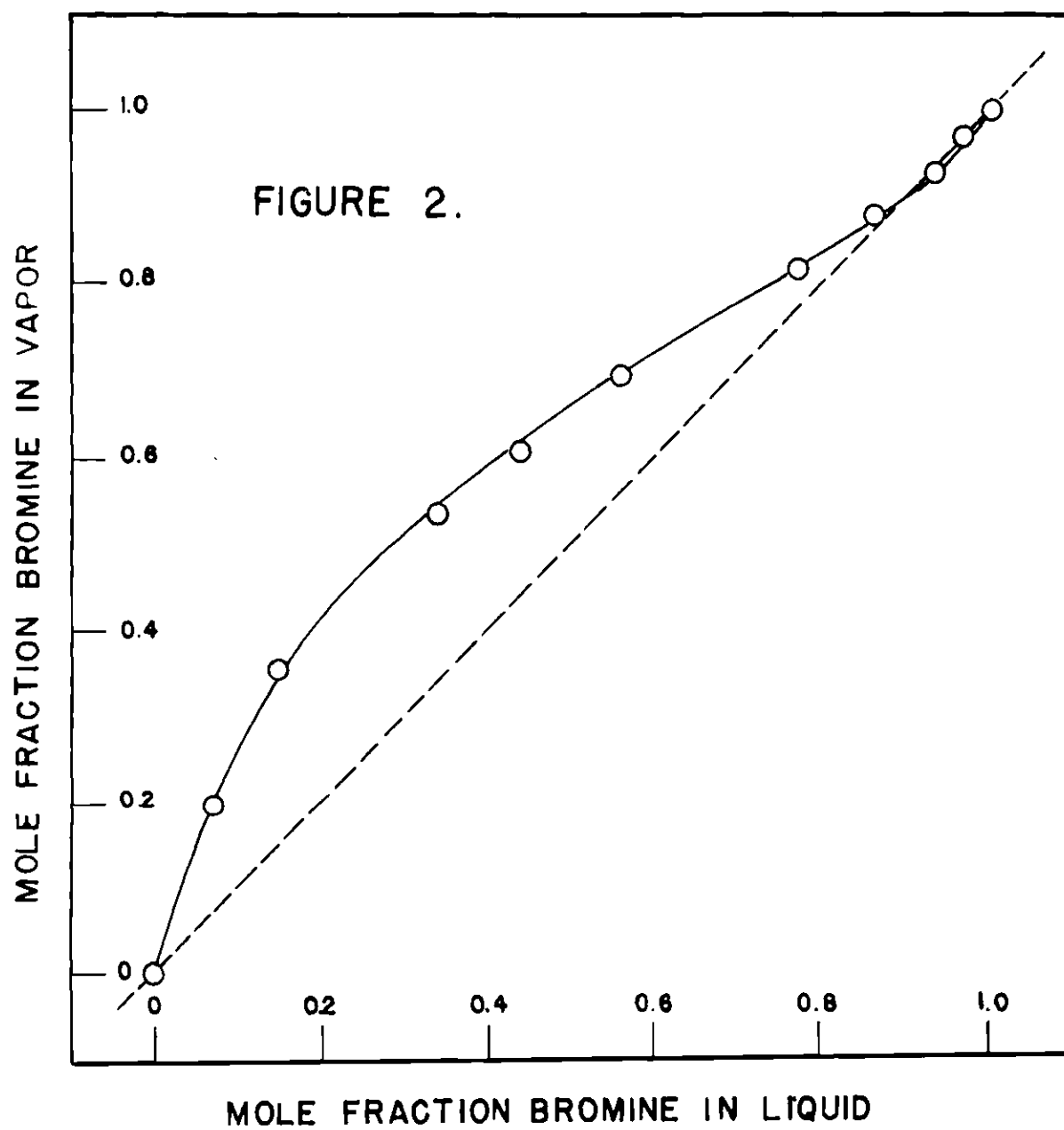
### TABLE AND FIGURES

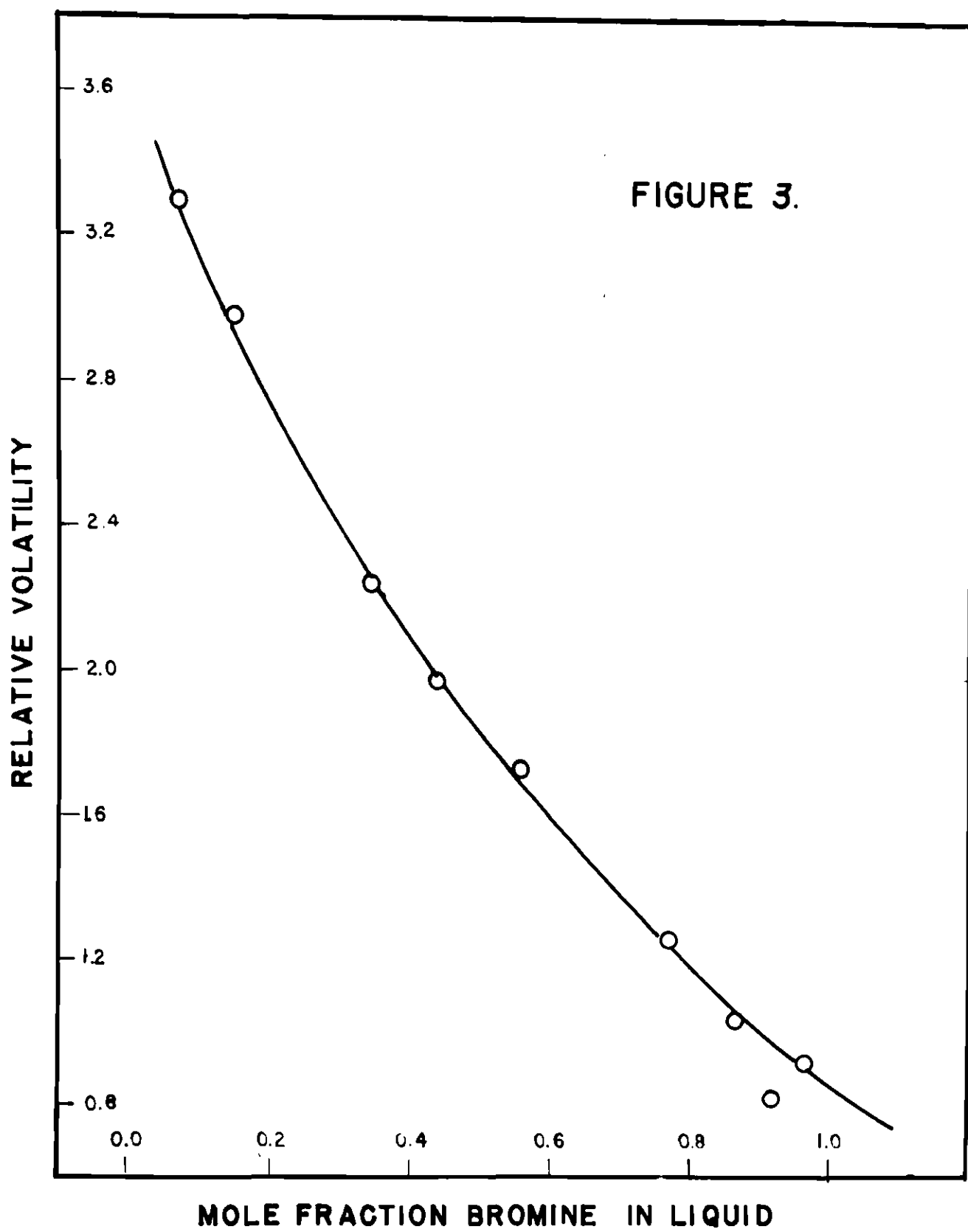
## APPENDIX I

TABLE I: Liquid-Vapor Equilibria Data for System Bromine-Carbon Tetrachloride

Temperature °C	Pressure mm.	Weight % Bromine in Liquid	Mole Fraction Bromine in Liquid	Weight % Bromine in Vapor	Mole Fraction Bromine in Vapor	Relative Volatility
58.0	741.2	100.0	1.0	100.0	1.0	--
57.9	738.1	97.0	0.969	96.7	0.966	0.906
57.7	736.8	94.2	0.940	92.9	0.927	0.809
57.9	736.8	86.9	0.865	87.8	0.874	1.095
58.1	736.8	77.7	0.771	81.6	0.810	1.272
59.9	734.6	56.1	0.558	69.7	0.690	1.758
61.2	734.6	45.0	0.441	61.5	0.606	1.953
63.1	738.5	35.0	0.342	54.5	0.536	2.247
68.6	734.3	15.6	0.151	36.1	0.353	3.059
71.7	736.7	7.25	0.070	20.5	0.199	3.301
76.0	738.5	0.0	0.0	0.0	0.0	--







**APPENDIX II**

**SAMPLE CALCULATION**

## APPENDIX II

## SAMPLE CALCULATION

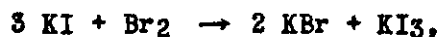
In order to illustrate the type of calculation involved in the analytical part of the experimental procedure, the following sample data and calculations are given:

Data

Weight of weighing bottle and KI solution	-- 60.1629 gms.
Weight of weighing bottle and KI solution + solution sample	-- 60.6975 gms.
Weight of sample	-- 0.5346 gms.
Milliliters of 0.1776 N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> standard solution	-- 30.60 ml.

Calculation

Since the reaction involved is



it is seen that one atomic weight of iodine is equivalent to one atomic weight of bromine. Thus, since the equivalent weight of iodine in iodometric titrations is one atomic weight, the equivalent weight of bromine is the same. The calculation is therefore as follows:

$$\begin{aligned} \text{Number equivalent weights bromine} &= \frac{\text{Normality of Na}_2\text{S}_2\text{O}_3 \text{ solution}}{\text{X No. of milliliters Na}_2\text{S}_2\text{O}_3} \\ &= \frac{30.60 \times 0.1776}{1000} = 0.005435 \end{aligned}$$

$$\begin{aligned} \text{Weight of bromine} &= \text{No. of equivalent weights} \times \text{equivalent weight} \\ \text{of bromine} &= 0.006475 \times 79.82 = 0.4338 \text{ gms.} \end{aligned}$$



$$\% \text{ Bromine} = \frac{\text{weight of bromine}}{\text{weight of sample}} \times 100 = \frac{0.4338}{0.5346} \times 100 = 81.14$$