

THE TERNARY SYSTEM -
IODINE, BROMINE, CHLORINE -
AT 29.8°C.

Thesis submitted as a requirement
for the degree of
MASTER OF SCIENCE

- by -

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October 1945

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I N T R O D U C T I O N

The binary systems of combinations of the three halogens - chlorine, bromine, and iodine - have been previously investigated and the existence of the following binary compounds was revealed: iodine monochloride, iodine trichloride, and iodine bromide. The existence of the two iodine chlorides was established beyond doubt; that of iodine bromide shown to be highly probable; and that of a fourth compound, bromine chloride, became controversial.

Prior to the present work, there has been no investigation of the ternary system. The importance of such an investigation lies in the fact that it would reveal the regions of existence of binary compounds, as well as the existence of any ternary compounds. While study of the isothermal solubility curves of the three halogens under consideration would give such information, there also remains the possibility of spectroscopic discovery of further binary compounds and even of ternary compounds. The earlier investigations referred to above were carried out from the point of view of thermal analysis, and had been thoroughly studied by the time of Karsten, who in 1907 was able to claim¹: "there is now almost entire clarity on the relationships between the pairs I-Cl, I-Br, and Br-Cl." Further development of interhalogen

investigation waited largely until the spectroscopic researches of Barratt and Stein and others, beginning in 1929.

The two avenues of exploration thus pointed out are thermal analysis and spectroscopic analysis. Research was carried out by the writer along the line of thermal analysis through a study of the isothermal solubility curves.

BASIC THEORY

(a) State of Equilibrium

All states and changes of equilibrium can be described qualitatively by the use of Gibbs' Phase Rule and Le Chatelier's Theorem. These two great enunciations were but the climax in a series of chemical attainments. Earlier workers such as Berthollet were perfectly cognizant of an equilibrium being set up in many reactions, beyond which point no change occurred. Not until Guldberg and Waage² stated their Law of Mass Action did it become possible to ascertain the conditions for homogenous systems. Since this was based on molecular theories, it could not, however, apply to systems of unknown molecular formations. A few years later, Gibbs³ introduced his Phase Rule which overcame this difficulty, and by which all cases of equilibrium, including heterogeneous equilibria, were surveyed and grouped.

(b) Phase Rule

Basically adopting the laws of thermodynamics, Gibbs assigned to a system three independent variables - temperature, pressure, and the concentration of the components of the system. He then stated, in a theorem now famous as the Phase Rule, the conditions of equilibrium to be a relationship between what he called the phases and the components of the system.

Phases are taken to mean any homogeneous, physically distinct and mechanically separable portions of a heterogeneous system. Liquids miscible in all proportions form a single phase. Two liquid layers would therefore be two phases. A mixture of gases, since completely miscible in all proportions, would be a single phase. Isomorphous crystals would give one phase, but two different types of crystals such as rhombohedral and hexagonal would be two phases. The amounts of the phase, or phases, present do not affect the equilibrium in any way.

The components of a system are defined as the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.

Each system was to have its conditions for equilibrium defined in terms of the three variables (temperature, pressure and concentration). Since Gibbs was dealing with equilibrium from a thermodynamical point of view, he also dealt with the thermodynamic criteria of equilibrium by means of thermodynamic potentials - a term used to indicate a certain characteristic of each component. These placed in equation form fixed the values of as many variables in the system as there were equations. Any variables left thus undefined were called degrees of freedom of the system. Findlay⁴ defines the number of degrees of freedom of a system as the number

of variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined.

Gibbs' deduction of the Phase Rule is not at all simple, and many alternative methods are now found. Any good text on thermodynamics will have some method suggested. All, however, give the Phase Rule in the form:

$$F = C - P + 2$$

where F = number of degrees of freedom

C = number of components

P = number of phases.

Certain simplifications are often used in the applications of this rule. The vapor phase is often neglected when constructing the freezing-point diagram for substances of comparatively low volatility. Additionally, constant pressure is assumed as one of the conditions of equilibrium when the work is carried out in the open laboratory.

Changes in equilibrium due to a change in the external conditions of temperature, pressure or concentration could not be deduced from the Phase Rule, however. The use of the theorem of Le Chatelier in this regard enhanced greatly the applicability of the Phase Rule. Molinari⁵ stated the theorem as follows:

"By every change of one of the factors which regulate a chemical-physical system in equilibrium, there are produced,

by the transformation in the system, actions which are opposed to the modifying factor."

Even with the use of this principle and the Phase Rule, there is no allowance for the so-called passive resistances of friction, capillarity, force of gravity, etc. With the additional limitation in mind that the phase rule applies only to conditions of true equilibrium (shown when the same conditions of equilibrium prevail when approached from both sides), it must still be remembered that the Phase Rule has extraordinary breadth of application.

(c) Types of Systems

Since this research is primarily concerned with the graphical expression of the phase rule in terms of two types of systems, these may be considered briefly.

(1) Binary systems, or systems of two components, when they exist in one phase would constitute a ternariant system, i.e., one with three degrees of freedom or where pressure, temperature and concentration must all be taken into consideration. When open systems are considered, i.e., systems under atmospheric pressure, the pressure is constant, and the system becomes bivariant which would allow for the existence of two phases. Such systems are usually represented on a plane section, with temperature as abscissa, and concentration as ordinates. The graphical expression is known as a temperature-concentration curve, or a t-x diagram.

Binary systems are usually classified in order to give a better means of discussion of the equilibria concerned. The order in which Findlay⁶ treats binary systems is an excellent classification in itself.

In considering his section dealing with solid solutions it might be preferable to use a classification made classical by Roozeboom⁷ in 1899 when he reviewed the different types of solid solution. Solid solution was the name given by van 't Hoff to a homogeneous crystalline mixture of the two components. Two substances soluble in each other are said to be "isomorphous", and the mixture is usually called an isomorphous solid solution.

(ii) Ternary Systems. Ternary systems, or systems of three components, imply through application of the Phase Rule that five phases are necessary for invariance. As the number of phases decreases, the variability of the system increases from one to four.

Representation of ternary systems graphically presents some difficulty. Most methods use a solid figure with the temperature as an axis. The development of methods was followed by Findlay⁸, and while several of those he mentions are still used, probably the most common is the triangular diagram developed by Roozeboom⁹. It consists of an equilateral triangle with lines ruled parallel to each side. The sides are divided into 100 parts, and the same scale is used for the binary systems on the side of the triangle. The

co-ordinates of a point ternary in composition are then measured parallel to the sides.

There are many types of ternary system, but none will be discussed here since the diagram obtained in this research was an isothermal diagram, and thus simple in conception.

(d) Isothermal Curves

The solubility relationships at constant temperature, or the isothermal solubility curves as they are known, are means of illustrating the change in solubility of one component by the addition of another component. In three-component systems they immediately give new light on the conditions of formation and stable existence of binary compounds in the presence of the three components, as well as on the existence of any ternary compounds.

For representing the isothermal relations in a ternary system, several methods can be employed. Three of these are discussed by Findlay,¹⁰ one of which is the triangular diagram mentioned above. This undoubtedly is the most useful since, as in the case of this research, the mutual relationships of all three components are dealt with in an equal manner.

When the states of equilibria between liquid and solid phases are plotted on the isothermal diagram curves will result depicting the solubility of the solid components or

solid compounds formed by any of the components. In all cases the "tie-line" which joins the two points representing the composition of the solid phase and the liquid phase will indicate, in the direction liquid to solid, what solid component or compound is saturating the liquid. The practical impossibility of complete separation of the solid phase from the mother liquor will mean, of course, that the tie-line would have to be extrapolated in order to give the actual composition of the solid phase.

(e) Methods of Determining the Equilibrium Curve

For determining the equilibrium curve of binary or ternary systems, many methods may be employed. These may be listed as thermal analysis, X-ray analysis, microscopic analysis, electrical conductivity, magnetic susceptibility, electrode potential, heat of mixture, intensity of reflection of light, atomic heats of components and compounds, specific volume of components and compounds. Only the first three allow of any completeness of information. In the case of determination of isothermal curves, however, it is necessary to use an analytical method which after the separation of the phases obtained at equilibrium under the conditions of temperature chosen, will give the composition of the liquid and solid phases. The liquid phase determinations will then give the curve of liquid solubility, and the solid phase determinations will indicate solid compounds or components, or

any case of solid solubility.

The method by which a determination of the composition of the solid phase in a system of three components, is due to Schreinemakers¹¹ originally, although developed further by Bancroft.¹² Since it is of importance to a consideration of the results of this research, it will be explained briefly here.

Consider that we are dealing with the aqueous solution of two salts (hence a three-component system) which can give rise to a double salt (equivalent of compound formation). Representing the solubility relations in a system of triangular co-ordinates, we would obtain an isotherm *adcb* (Fig. 1).

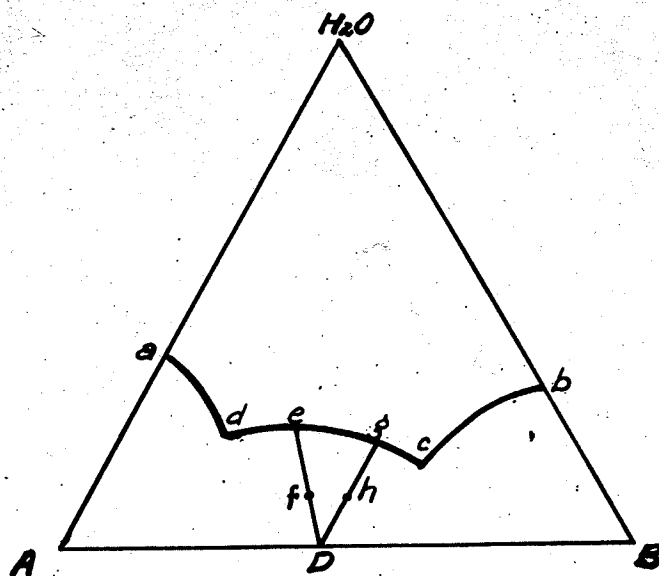


Fig. 1.

In the above diagram the two components, A and B, can form a double salt of composition D. The point a represents the solubility of the salt A, b the solubility of the salt B, and d and c represent solutions which are in equilibrium with pure A and double salt, and pure B and double salt respectively.

Consider, then, that the double salt is in equilibrium with the solution at the definite temperature chosen, and that the composition of the solution is represented by the point e. The greater part of the solution is now separated from the solid phase, and the latter, together with the adhering mother liquor, is analysed. The composition (units of concentration as shown) would be represented by a point f on the line eD, where D represents the composition of the double salt. This is true since the composition of the whole mass must lie between the composition of the solution and that of the double salt, no matter what may be the relative amounts of the solid phase and the mother liquor. Similarly the analysis of a solution of different composition in equilibrium with the same double salt, and also the mixture of solid phase and solution, would give two other points such as g and h, and the line joining them would also pass through D. The method of finding the composition of an unknown double salt (or compound) consists, therefore, in finding the position of two lines such as ef and gh. The point of intersection of these lines, then, gives the composition of the

double salt (solid phase). If the solid phase is a pure component (anhydrous), the lines will all pass through a corner of the triangle; if it is an anhydrous double salt as given above, the lines will intersect at a point on the side AB of the triangle; if it is a hydrated component, they will intersect at a point on the side A-H₂O or B-H₂O, of the triangle; and if it is a hydrated double salt (a ternary compound) the point of intersection will lie within the triangle.

It should also be noted that, working with open systems, and neglecting the vapour phase means that for isothermal determinations there is only one degree of freedom. This univariant system would then allow of four phases (solid and liquid). Any more would cause an invariant point.

PREVIOUS INVESTIGATION

(a) The System Iodine-Chlorine

For over a century it has been definitely known that at least two crystalline substances were formed from the two elements iodine and chlorine. The first complete investigation of the system iodine-chlorine, however, waited until after Roozeboom's famous work on the equilibrium of two bodies combined in a system, when, using this method of investigation, Stortenbeker^{13,14} made his classical researches on iodine and chlorine. Stortenbeker not only determined many of the exact properties of the two compounds previously known, but he identified them without question as the trichloride and monochloride of iodine; and even made complete investigation of the two allotropic forms of the monochloride which were previously unknown. These latter he termed $\text{ICl}\alpha$ and $\text{ICl}\beta$, and showed that $\text{ICl}\alpha$ was the stable form with the higher melting point. While his investigation stated the conditions of existence of these compounds, he was also able to claim that no other compounds of iodine and chlorine existed as had been claimed by earlier investigators largely on theoretical grounds.

This first clarification on the relationships of the halogens with one another, has needed little amplification to this day. A clearer insight into the stability of ICl in liquid and gaseous state was given by Karsten,¹⁵ and Walden¹⁶ gave more detailed data on the states of stable existence of

the monochloride. Beyond these points the essential work of Stortenbeker still stands alone.

It is, then, worth noting that the solid substances with which to be concerned in any isothermal investigation would be iodine (m.p. = 113.5°),¹⁷ iodine monochloride ($\text{ICl}\alpha$, m.p. = 27.2° , $\text{ICl}\beta$, m.p. = 13.9°),¹⁸ iodine trichloride (m.p. = 101°),¹⁹ and chlorine (m.p. = -101.6°).²⁰

(b) The System Bromine-Chlorine

The existence of a chloride of bromine has been long mooted, and beginning with the work of Balard²¹ and Loewig²² who first claimed to describe it, considerable controversy has taken place. Bornemann²³ attempted to determine its formula and claimed it to be $\text{BrCl} \cdot 10\text{H}_2\text{O}$. His work was repeated by Lebeau²⁴ who found the substance to be only a simple mixture both in the liquid and crystalline state, by a determination of a m.p. curve. However, its existence, along with what was thought to be the trichloride, was claimed by Thomas and Dupuis²⁵ following their work with the reaction of liquid chlorine on bromine.

More reliable thermal investigations were then commenced, and careful analytical determinations of the melting and freezing point curves of mixtures of chlorine and bromine from 100% chlorine to 100% bromine were made by Karsten.²⁶ His work bore out the claims of Lebeau and he completely refuted the inadequate claims of Thomas and Dupuis. In

addition to the m.p. and f.p. curves Karsten made several isothermal determinations of liquid and solid phases in equilibrium which agreed closely with his thermally determined points. He then concluded that in the solid state bromine and chlorine formed a continuous series of mixed crystals. He also determined the complete boiling-point curves and on that basis claimed it unlikely that compounds would exist in vapor form. This can be substantiated by theoretical considerations of Roozeboom,²⁷ which, with the later help of the phase rule, indicated the influence which the existence of partly dissociated compounds in liquid and vapor state has on the vapor pressure or boiling-point curve. The work of Karsten on freezing-point determinations was duplicated by Butler and McIntosh²⁸ who merely restated the claim against the existence of BrCl because of the form of the freezing-point curve.

While the work by thermal analysis seems to indicate that no compound exists, Lux²⁹ has introduced a new note in his claim to have obtained BrCl by slow distillation and fractional condensation of a mixture of equal parts of Cl and Br. The compound thus obtained (at -90°) shows a higher vapor pressure than that of Br, and on analysis showed a Cl:Br ratio of 1:1.

Optical analysis for the most part tends to support the existence of a compound BrCl. Beginning with the data given by Barratt and Stein³⁰ who obtained a new absorption band which they credited to BrCl, much confirmatory evidence

was gathered. An excellent outline of the investigations pursued is given by R.J. Meyer in "Gmelin's Handbuch".³¹ Later work along the same line has more definitely established the dissociation constant of BrCl as being very low (0.11 at 28°)^{32,33} and constant over a wide temperature range.

Organic reactions have also tended to verify the existence of BrCl . The most outstanding example is in regard to action on aliphatic diazo compounds, which, according to Taylor and Forscey,³⁴ indicated about 80 molecular per cent of the BrCl derivative and 10 molecular per cent each of the Cl and Br derivatives.

Probably the closest approach to its isolation was the preparation of its hydrate $\text{BrCl} \cdot 4\text{H}_2\text{O}$ (Anwar-Ullah³⁵), although its melting point has been given as -66° .³⁶ If this latter figure is approximately correct it is obvious that under the conditions of this research (determinations at 30°) there is not likely to be any compound of bromine and chlorine distinguishable thermally.

(c) The System Iodine-Bromine

Balard's³⁷ historic work on bromine gave the first indication of there being compounds of iodine and bromine. His observations gave indication of two compounds, and were confirmed by C. Löwig³⁸ who assumed that the liquid rich in bromine was IBr_3 and the one poor in bromine was IBr . Lagermarck³⁹ prepared crystals from a mixture of the two

elements by equivalent weights. This synthesis was repeated by Bornemann,⁴⁰ who also analysed the product and found it approximated the monobromide.

In 1905 the whole system iodine-bromine was classically investigated by Meerum-Terwogt⁴¹ who showed that the liquidus and solidus freezing-point curves of mixtures of iodine and bromine nearly coincide when the ratio of equivalent weights is $I:Br = 1:1$. The conclusions reached from his work could only be taken to the point of claiming a continuous series of isomorphous mixed crystals extending from pure iodine to a mixture corresponding to iodine bromide, as well as the strong likelihood of the existence of iodine bromide in solid and liquid state, with it becoming almost entirely dissociated in the vapour state. Certain verification of these claims was made thermodynamically by Ruer,⁴² and also much later by Kruyt and Helderman. The latter claimed⁴³ that the compound IBr existed on the basis of the occurrence of the two maximums in the P-T-concentration diagram for systems with continuous series of mixed crystals. Certain work has been carried on also on the equilibrium in the vapor state for the formation of iodine bromide from its elements.^{44,45,46} A further step in the verification of iodine bromide as a chemical compound was made by Wright⁴⁷ who found that an equimolecular solution of iodine in bromine lowered the vapour pressure of bromine as if its chemical composition was IBr .

Electrochemical studies have also shown its presence in solution.⁴⁸ In summary, it is clear that a great deal of the difficulty in establishing IBr as a compound has been because of its endothermic unstable nature, and its great dissociation even at 30°.

While the existence of a compound of iodine and bromine with high bromine content was first mentioned by Balard⁴⁹ and Löwig,⁵⁰ it was Bornemann⁵¹ who claimed that IBr₃ did not exist, and that the previous claim was based merely on a solution of IBr in Br₂. Further evidence against the existence of such a compound was also given by Reade⁵² on the basis that no polyhalide group contained the IBr₃ group or a dibromine iodide group; and also by Plotnikow and Rokotjan⁵³ because of the formation of the positive iodide ion in a solution of IBr in bromine. Further proof was given by the fact that the absorption spectra obtained for a solution of IBr in Br₂ corresponding to IBr₃ is exactly the same as the sum of the spectra of IBr and Br₂.⁵⁴ Contrary evidence has been entered lately as Forbes and Faull⁵⁵ claim strong electrometric evidence for the presence of IBr₃ or its complex ion IBr₄⁻ in solution where $[Br] = 3[I]$.

It was thus generally concluded that for the purposes of this research the only compound likely to appear in connection with isothermal determinations at 30° would be IBr (with a melting point of 41°C as given by Terwogt⁵⁶), and that this would form a continuous series of mixed crystals with iodine.

(d) The Polyhalogen Compounds

Since there are so few combinations of the halogens with each other it is interesting to note that the ions of the halogens seem particularly active in forming compounds with the halogens. These give rise to such compounds existing in solution as the KI_2 claimed by Jakowkin,⁵⁷ as well as many complex anions with various combinations of two, or even three, of the halogens.

While much of the emphasis on polyhalides seems to be in the field of aqueous solutions, there has also been some considerable investigation on solid solutions of metallic polyhalides. Nowhere, however, has there been any sign of a consideration of the three elements, iodine, bromine, and chlorine, forming a ternary compound (or a halogen polyhalide as this field of literature would name it).

The closest approach to any regard for a ternary system is contained in the study by Plotnikow and Rokotjan⁵⁸ of the system $Br-ICl_3$. While their whole concern was with the electrical conductivity of bromine solutions of iodine and of iodine trichloride, they, of necessity, made determinations of the solubilities of both I_2 and ICl_3 in bromine.

Discussion of this in comparison with the results of this research will be detailed later.

Since the only known compounds occurring within the three binary systems discussed above which exist as solids at ordinary temperatures are iodine bromide, iodine monochloride

and iodine trichloride, it was decided that first isothermal determinations of the ternary system should be carried out at such temperatures. This would bring iodine into the picture also, and hence in order to further simplify the first isothermal diagram the temperature of 30°C was chosen. This point was above the m.p. of the iodine monochlorides and hence further reduced the number of solid phases or solid phase constituents it would be possible to obtain.

APPARATUS AND ANALYSIS

(a) Purity of Materials

The iodine used was of U.S.P. XII grade (resublimed crystals).

Bromine used was Mallinckrodt Bromine, conforming to N.F. V specifications.

Chlorine was obtained as a commercial grade in small cylinders from C.I.L. It was then washed with distilled water (two wash bottles), and bubbled through saturated CuSO_4 solution to remove any traces of hydrogen chloride as recommended by F. Stolba.⁵⁹ The gas was then dried by passage through concentrated sulphuric acid.

(b) Materials for Analysis

The silver nitrate used was U.S.P. standard reagent. It was pulverized in an agate mortar, and dried over concentrated sulphuric acid for a week. Standard N/10 solution was made by dissolving an exactly weighed amount of the powdered dry salt in distilled water, kept at room temperature (16.9888 grams per litre).

For standardization purposes the KI, KBr and KCl used were all of U.S.P. standard grade.

The barium nitrate to be used in the analysis for preventing any of the bromide or chloride being carried down with the iodide was of the standard reagent grade.

Certain analyses were made with barium nitrate made from the action of nitric acid on barium carbonate and

recrystallized from distilled water. No observable differences were found in the latter case.

(c) General Apparatus

Since isothermal determinations to give accurate data on any system require a very close temperature control, it was necessary to ascertain and maintain the temperature within close limits during the attainment of equilibrium by any ternary system. The temperature selected for this research was 30°C for the reasons outlined earlier.

A cylindrical glass vessel containing water was used as the thermostat. A top layer of kerosene was placed on the water to reduce evaporation and surface cooling. The water was stirred by means of a small motor-driven metal stirrer which was maintained at a slow rate.

Sufficiently good temperature control was obtained by intermittent heating with atmospheric cooling. The heating system was a 50-watt electrical element contained in a copper coil immersed in the bath. The heating current was controlled by means of a solenoid-operated mercoid switch which was actuated by a mercury thermoregulator. This method enabled a temperature control better than $\pm 0.05^{\circ}\text{C}$. to be maintained.

The actual temperature was measured with a thermometer graduated to 0.01°C . and calibrated directly against a standard correction thermometer. With this arrangement and applying the correction, the temperature remained at $29.80 \pm 0.05^{\circ}\text{C}$.

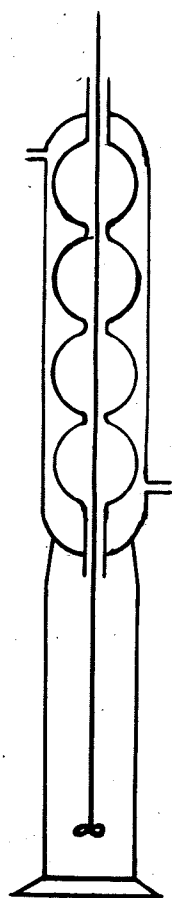
throughout the period of the research.

The container first used to hold the halogen system was a glass cylinder of 450 ml. capacity, with an inner diameter of 1 1/4 inches, and an outside tapered ground glass top (see Figs. 2 and 3). This was later supplemented with a number of small cylindrical glass bottles of approximately 250 cc capacity with large ground-glass stoppered mouths.

With these containers a system could then be made up of volume and weight (100 to 250 grams) sufficient to allow of good separation of phases and proper sampling, and also make for ease of efficient stirring within the container.

The glass containers were clamped within the bath and surmounted by a glass condenser filled with cold water. A long glass stirring rod was inserted in the condenser and connected to a small variable speed motor.

The glass container was part of an all-glass unit constructed especially for efficient separation of solids and liquids (Fig. 3). The glass container was fitted by a ground-glass cap with a 3/16" outlet, and a 3/16" ring seal projecting inside about 6 inches where it was flared out to contain a circular piece of sintered glass about 1/2 inch in diameter and 3/16" thick. The outside connection of the ring seal was sealed similarly to another cap and glass container of similar tapered ground-glass design. The other 3/16" outlet from this second cap could be attached to a vacuum pump. Thus, by applying vacuum the liquid phase could be led by suction from



All-glass units.

FIG. 2

Container for System.

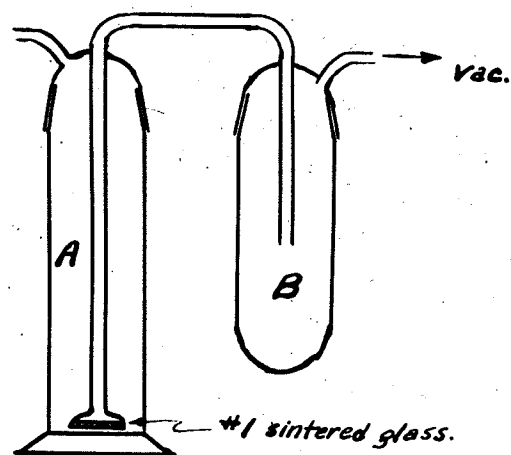


FIG. 3

*Apparatus for Separation
of Phases.*

vessel A through the sintered glass and connected tubing into vessel B from where a sample could then be taken. The solid phase remaining in vessel A could be sucked quite dry in a very short time. A satisfactory source of vacuum was found to be a small glass water pump.

(d) General Procedure

(1) Making up Systems. The first system was made by dissolving iodine in bromine at a composition which, according to Terwogt⁶⁰ would give a solid and liquid phase, i.e. slightly more iodine in weight per cent than is soluble in bromine at 30°. In making further systems dry chlorine was bubbled through a glass tube drawn to a jet into the previous system until length of time and rate of bubbling gave an indication of percentage added. Better results were obtained by weighing the container before and after addition of chlorine, even though this did not allow for the considerable loss of bromine, because of its high vapour pressure. In addition to the chlorine, some iodine was added.

The system was thus adjusted until solid phase was obtained. As the diagram began to take shape, better judgment could be used, and calculated ingredients enabled a suitable composition to be obtained more easily. The system was then heated until all solid dissolved (in warm water 40° to 50°), and was finally placed in the 30° bath to attain equilibrium. The glass stirrer was inserted and put into motion for at

least 12 hours.

In order to obtain the systems on the binary I_2-Cl_2 axis, iodine trichloride was made according to the method of Booth and Morris.⁶¹ Finely powdered iodine was added slowly to a flask containing liquid chlorine condensed from a cylinder by means of solid CO_2 in acetone as a cooling liquid. The flocculent orange ICl_3 was freed from excess chlorine by evaporation at room temperature, and kept in a dry glass-stoppered flask. The trichloride thus synthesized was used in order to obtain ternary systems of composition above 10% in chlorine and iodine.

All work was carried out within a fume cupboard under strong draft. The purifying train for the chlorine was contained in the fume chamber. The bromine was measured by volume, and the iodine by weighing on a rough balance.

(2) Separating Phases and Sampling. After a system (150 to 250 grams in weight) had remained in the 30° bath for at least 24 hours, the stirrer and condenser were removed, and the sintered glass end of the separation apparatus (Fig. 2) inserted. The glass tube outlet from the receiving vessel B was attached to the vacuum, and the liquid phase sucked through. By pressing the flat sintered glass surface down tightly on the solid remaining in the glass container, as much mother liquor as possible was sucked out. Care was taken to leave the vacuum on for only a very short period of time. Separation took place usually within 30 to 60 seconds, and in consequence the vapor loss was kept to a minimum.

The glass vessel containing the liquid phase was immediately placed in a beaker containing water at 30°C. A sample was taken from it by means of a small pipette attached by rubber tubing to the vacuum pump. About 8 cc. of liquid were drawn into the pipette and then about 2 1/2 cc. were allowed to run into a tared ground-glass stoppered weighing bottle.

The solid phase was sampled immediately after the separation was complete. A long piece of glass rod flattened into a spoon at one end sufficed to remove some of the solid from the bottom of the original container. From 5 to 10 grams were placed in a tared weighing bottle, which was thereupon tightly stoppered with a ground-glass top.

The remaining liquid and solid were placed again in the container and were used in many cases as a basis for another system of different overall composition.

(3) Preparation of Sample for Analysis. The samples of the solid and liquid were weighed and then individually "drowned" in caustic soda solution. This was accomplished by inverting the weighing bottle and placing its mouth beneath the surface of 500 cc. of 10% sodium hydroxide solution contained in a large glass funnel. The funnel was stoppered by means of a piece of glass extending from above the top of the funnel down into the neck where a tight seal was made with a short piece of rubber tubing. The neck of the funnel extended down into a 1-litre volumetric flask. When the sample had been

released into the caustic soda solution, the glass rod stopper was removed and the whole contents of the funnel then ran into the volumetric flask. The glass rod stopper, weighing bottle and top, and the inside of the funnel were then carefully washed down with distilled water. The flask was removed from beneath the funnel and the contents made up to exactly one litre with distilled water at room temperature.

Careful use of this technique enabled an accurately weighed sample to be treated with caustic soda solution with no loss whatsoever by vapour or otherwise. With one or two samples of high bromine and chlorine content, it was found very difficult, however, to carry out the "drowning" without a slight vapor loss.

According to Meller,⁶² the best evidence points to the formation of the hypohalites along with small amounts of the free element remaining in solution when the elements are brought into contact with dilute and/or cool solutions of caustic soda or potash. However, hot and/or concentrated solutions of the hydroxides produce the halates very quickly. There is also some indication of halide formation. While there seems to be no direct evidence regarding the effect of caustic soda solution on the three halogens together, it was assumed that they might be present in any or all of the states mentioned. Reduction to the halides was then necessary for analysis.

The caustic soda solution of the halogens was carefully mixed in the litre flask, and a 100 ml. aliquot was then

removed by means of a small volumetric flask calibrated at the 100 ml. mark to give 99.98 ml. The small flask was emptied into a 250 cc. beaker and rinsed three times with distilled water. About 3 grams of powdered zinc metal were added and the solution was boiled gently for 20 minutes. It was then made slightly acid to litmus with glacial acetic acid, and boiled for another 20 minutes. The zinc was filtered off and carefully washed into the same beaker as the filtrate. The filtrate was made up to 600 cc. with distilled water and the sample was then ready for analysis.

The above reduction proved to be entirely satisfactory, and was adapted from methods^{63,64,65} recommended as successful. Slight adaptations were necessary because of the barium nitrate and/or silver nitrate required in the analytical procedure.

(e) Method of Analysis

The method used for this analysis was potentiometric, and had not previously been developed to the extent where all three halogens could be simultaneously estimated. The essence of the method is given by Stock and Stahler⁶⁶ and outlined by them for volumetric determination of chlorine and iodine in neutral solution of potassium chloride and potassium iodide. The method depends essentially on the rate of change in the difference of potential between the solution and a suitable electrode. The reaction is followed volumetrically, and during a titration the concentrations of the ions taking part in the

reaction are altered at a comparatively enormous rate in the neighbourhood of the endpoint of the reaction. Thus if the titration is plotted against the measurement of the potential, a curve is obtained which has a point of inflexion at the endpoint.

Since the above method of analysis was recommended for titration of chloride and iodide by silver nitrate, it was felt that there would be sound theoretical basis for including bromides. The change in emf., using silver electrodes, would depend upon the concentration of Ag^+ ions in solution. Since the solubility products of silver iodide, bromide and chloride are respectively 10^{-16} , 10^{-13} , and 10^{-10} , it follows that the halides will be precipitated in this order, the endpoint of each precipitation being indicated by a maximum in the emf. With rapid titration it is necessary to prevent some of the chloride and bromide from being carried down with the silver iodide. This was done by adding barium nitrate which was adsorbed by the iodide in place of the other halides.

The apparatus required included a complete arrangement for measurement of emf. A Leeds and Northrup student-type potentiometer with a galvanometer of equal sensitivity were set in a circuit as shown in Figure 4. A standard cell was included for calibration purposes. The silver electrode used is illustrated in Figure 5.

The reference electrode B was a silver wire 0.5 mm. in diameter, inserted in the 1-mm. diameter bore of a 12 cm.

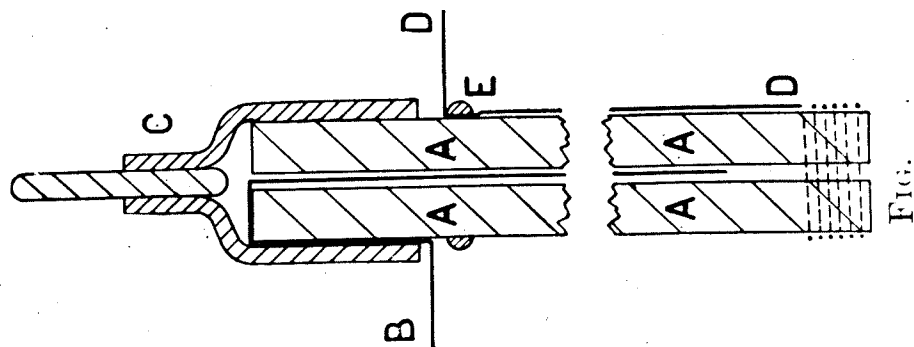


FIG.

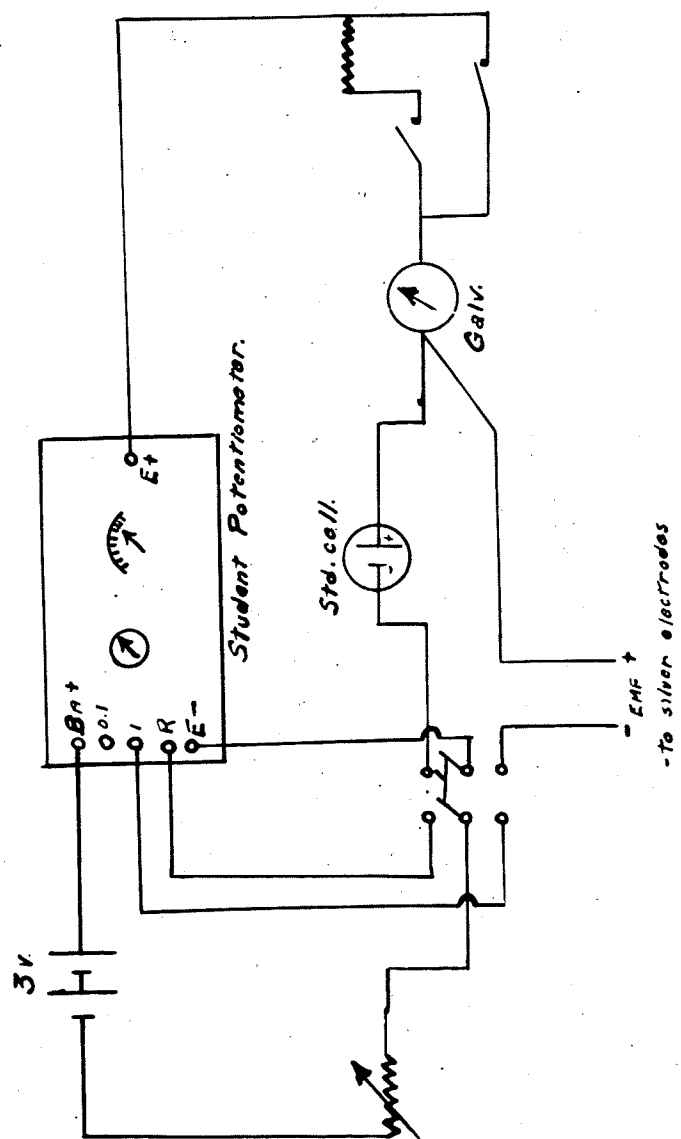


FIG. 4

Circuit for Electrometric Analysis.

length of glass capillary tubing A whose wall thickness was about 3 mm. in such a manner that the lower end of the wire remained about 20 mm. above the bottom of the capillary tube. The other end of the wire was bent around the tube as shown and was held in place by a short well-fitting piece of rubber pressure tubing which was closed at the top by a short length of glass rod. The indicator electrode D was also of 0.5 mm. diameter silver wire and was wound several times around the lower end of A, and fastened by a rubber band E.

This electrode, a motor-driven glass stirrer, and a 50-ml. burette were mounted so that the beaker containing the solution to be titrated could be brought up under them. The litre beaker with the 600 cc. of solution was put into position and 30 grams of pulverized barium nitrate added and dissolved with stirring. The electrode was then immersed in the solution, whereupon the liquid entered the capillary and was drawn up around the lower end of the reference electrode. Since it was essential that the composition of this liquid in the capillary remain unchanged during the titration, care was taken to maintain the height of the column of liquid in A as initially obtained.

There is no difference in potential before the addition of silver nitrate (N/10). The first addition was usually made in 10 cc. portions, and the emf. compensated by means of the potentiometer. It was sometimes possible to make a steady continuous addition, with a constant potentiometer adjustment until

approaching the endpoint. The silver nitrate solution was then added dropwise, the volume recorded, and the emf. also noted. The change in emf. per ml. of silver nitrate added was then calculated. The volume recorded for the greatest change per ml. was taken as the endpoint. For each titration there thus resulted three endpoint determinations. Calculations were then made from the volume of 0.1N silver nitrate for an equivalent amount of weight of chlorine, bromine and iodine.

It was found necessary to stop the stirrer before each reading on the potentiometer was taken, and thus give time for the precipitate to settle. The electrode was washed with distilled water and dried with filter paper after each determination. The reference electrode was removed every few determinations and cleaned carefully to remove a coating of the halides which seemed to be formed on its contact surface.

Results obtained justified its use for all three halides since an endpoint was easily observable in all cases.

EXPERIMENTAL RESULTS.(a) Analytical Accuracy

The method of analysis used for accurate determinations of the concentration of chlorine, bromine and iodine in mixtures of the three was tested for accuracy in its determination of a mixture of low chlorine content. The results obtained are shown in Table I below. The first three of these determinations were made on standard N/10 solutions to which 30 grams of barium nitrate were added, the whole made up to 600 cc. with distilled water, and then analysed.

A further check was made on analytical technique by several reanalyses of the solutions made from the solid and liquid phase samples. Typical results are given below in Table II.

TABLE IPotentiometric Determinations of Halide Solutions

Results are given for No.1 in cc. of 0.025N AgNO₃
 No.2 in cc. of 0.0125N AgNO₃
 No.3 in cc. of 0.1N AgNO₃

	<u>No.</u>	<u>Calculated</u>	<u>Found</u>	<u>% Error</u>
I ⁻	1	19.98	19.99	+0.05
	2	39.96	40.05	+0.2
	* 3	24.97	24.96	-0.04
Br ⁻	1	20.02	19.93	+0.5
	2	40.04	40.30	+0.6
	3	25.03	24.99	-0.2
Cl ⁻	1	19.98	20.18	+1.0
	2	2.00	2.20	+10
	3	2.00	2.28	+14

*Results for No.3 are the average of two determinations with a mean deviation from the mean of less than 0.5% in each case.

T A B L E I I
Typical Repeat Analysis on Same Solution

		<u>Endpoint of Titration in cc. of N/10 AgNO₃</u>		
		<u>Iodide</u>	<u>Bromide</u>	<u>Chloride</u>
A.	1.	23.45	52.08	55.10
	2.	23.37	52.07	55.12
B.	1.	27.58	68.46	74.26
	2.	27.65	68.59	74.22

Note: A and B are the solid and liquid phases respectively of System 2 (see Table V for calculated weight per cents).

(b) Check on Total Halogen Content of Systems

The method of preparing the sample for analysis involved a weighing of the sample (both liquid and solid phase) before analysis. Since the analysis gave a determination of all three halogens present, it was thus possible to get a check on the total for the determination. The comparative results obtained are given in Table III, and are shown in such detail because of their possible value in any further work carried out on the analytic method used here.

T A B L E I I I

Total Weight of Halogens in Systems

All values in grams

System and Phase	Iodine	Bromine	Chlorine	Total	By Weighing Total	% of Actual Weight
1-L	0.0932	0.0883	-	0.1825	0.1808	100.44
1-S	0.3656	0.2805	-	0.6461	0.6654	97.10
2-L	0.3501	0.3268	0.0206	0.6975	0.6775	100.95
2-S	0.2976	0.2289	0.0107	0.5372	0.5299	101.38
3-L	0.3521	0.3190	0.0222	0.6933	0.6751	102.70
3-S	0.4880	0.3711	0.0219	0.8810	0.8612	102.30
4-L	0.2949	0.2552	0.0224	0.5725	0.5539	103.36
4-S	0.6257	0.4643	0.0233	1.1133	1.0932	101.84
5-L	0.3830	0.2245	0.0390	0.6465	0.6285	102.86
5-S	0.4177	0.2414	0.0234	0.6825	0.6751	101.09
6-L	0.4866	0.2233	0.0528	0.7627	0.7437	102.55
6-S	0.7028	0.3376	0.0459	1.0863	1.0725	101.29
7-L	0.4586	0.1845	0.0507	0.6938	0.6802	102.00
7-S	0.3913	0.1690	0.0295	0.5898	0.5776	102.11
8-L	0.6152	0.1694	0.0722	0.8568	0.8488	100.94
8-S	0.4717	0.1371	0.0424	0.6512	0.6347	102.60
9-L	0.5491	0.1204	0.0531	0.7226	0.7110	101.63
9-S	0.6395	0.1327	0.0871	0.8593	0.8456	101.62
10-L	0.6545	0.0951	0.0922	0.8418	0.8322	101.15
10-S	0.7028	0.1044	0.0603	0.8675	0.8628	100.54
11-L	0.7265	0.0686	0.0993	0.8944	0.8907	100.42
11-S	0.3622	0.0288	0.0232	0.4142	0.4058	102.07
12-L	0.9333	0.0504	0.1397	1.1234	1.1215	100.17
12-S	1.1290	0.0480	0.0831	1.2601	1.2528	100.58
13-L	0.7452	-	0.1346	0.8798	0.8766	100.37
13-S	0.5679	-	0.0415	0.6112	0.5973	102.33
14-L	0.4572	-	0.1726	0.6298	0.6275	100.37
14-S	0.5587	-	0.2967	0.8554	0.8693	98.40
15-L	0.4521	0.0261	0.1634	0.6466	0.6406	100.94
15-S	0.4416	0.0181	0.2422	0.7019	0.7068	99.31
16-L	0.2952	0.0543	0.1073	0.4568	0.4467	102.26
16-S	0.4482	0.0466	0.2482	0.7430	0.7399	100.42

System and Phase	Iodine	Bromine	Chlorine	Total	By Weighing Total	% of Actual Weight
17-L	0.4113	0.0994	0.1534	0.6641	0.6650	99.86
17-S	0.1394	0.0183	0.0932	0.2509	0.2392	104.89
18-L	0.4146	0.1127	0.1624	0.6897	0.6827	101.03
18-S	0.3379	0.0489	0.2164	0.6032	0.5943	101.50
19-L	0.3505	0.1289	0.1427	0.6221	0.6070	102.49
19-S	0.4107	0.0922	0.2514	0.7543	0.7302	103.30
20-L	0.3187	0.3517	0.1916	0.8620	0.8888	96.98
20-S	0.4018	0.1566	0.2713	0.8297	0.8437	98.34
21-L	0.2192	0.2661	0.1377	0.6230	0.6360	97.96
21-S	0.2439	0.0673	0.1872	0.4984	0.4913	101.45
22-L	0.2227	0.6084	0.1578	0.9889	1.0219	96.77
22-S	0.2105	0.1913	0.1810	0.5828	0.5764	101.09

(c) Attainment of Equilibrium in System

In order to fulfil the theoretical requirements that equilibrium was obtained in the systems analysed, they all remained in the constant temperature bath for at least 24 hours. That equilibrium was thus obtained was proven by approaching equilibrium from both sides and ascertaining the composition of the liquid and solid phases present in each case. A single system was chosen and divided into two parts. The first part was heated until it had become entirely liquid and was then placed in the constant temperature bath. The second part was cooled until it was largely solid phase, and it was then similarly put into the 30° bath. The solid and liquid phases of each were analysed, with the results appearing in Table IV below.

T A B L E I V
Attainment of Equilibrium in System

Weight Per cent						
	Solid Phase			Liquid Phase		
	I	Br	Cl	I	Br	Cl
System A						
(1 day)	68.02	26.32	5.66	67.52	25.04	7.44
(3 days)	66.98	26.31	6.71	66.78	24.93	8.30
System B						
(1 day)	69.02	25.45	5.52	67.76	25.20	7.03

Note: Systems A and B were of identical overall composition initially. System A was brought to equilibrium from all liquid side, and B from all solid side. In each case the final state of equilibrium gave only a relatively small amount of solid phase in a large amount of liquid.

(d) Isothermal Diagram

The most important results of this research are given in Table V, and consist of the composition in weight per cent of various systems where the liquid and solid phases were in equilibrium. These results are also plotted graphically (Figure 6) and form the isothermal diagram for the ternary system at 29.8°C.

TABLE V

Composition of Liquid Phase			Composition of Solid Phase			Nature of Solid Phase	
(Weight per cent)			(Weight per cent)				
I ₂	Br ₂	Cl ₂	I ₂	Br ₂	Cl ₂		
1.	51.45	48.55	-	56.59	43.41	-	I-Br mixed crystals
2.	50.24	46.85	2.91	55.34	42.66	2.00	same
3.	50.79	46.01	3.20	55.40	42.12	2.48	"
4.	51.52	44.56	3.92	56.20	41.71	2.09	"
5.	59.24	34.73	6.03	61.20	35.37	3.43	"
6.	63.80	29.27	6.93	64.70	31.07	4.23	"
7.	66.11	26.59	7.30	66.35	28.65	5.00	"
8.	71.80	19.77	8.43	72.43	21.06	6.51	"
9.	74.42	15.44	10.14	76.00	16.65	7.35	"
10.	77.76	11.29	10.95	81.00	12.04	6.95	"
11.	81.23	7.67	11.10	87.45	6.99	5.61	"
12.	83.07	4.49	12.44	89.59	3.81	6.60	"
13.	84.72	-	15.28	93.23	-	6.79	I ₂
14.	72.60	-	27.40	65.30	-	34.68	IOCl ₂
15.	69.91	4.04	26.05	62.92	2.58	34.50	same
16.	64.63	11.89	23.48	60.32	6.27	33.41	"
17.	61.94	14.96	23.10	55.58	7.29	37.16	"
18.	60.11	16.34	23.55	56.03	8.11	35.86	"
19.	56.35	20.72	22.93	54.45	12.22	33.33	"
20.	36.98	40.80	22.22	48.43	18.87	32.70	"
21.	35.18	42.71	22.11	48.93	13.50	37.57	"
22.	22.52	61.52	15.96	36.13	32.82	31.05	"

DISCUSSION OF RESULTS

The results tabulated for the method of analysis used (Table I) indicate that when the three constituents are present in approximately mol-equivalent amounts, an accuracy well within 1% is obtainable. However, with small amounts of chlorine the per cent error is considerably increased for this particular determination.

It must be noted that the effect of any error in titration values could be considerably reduced in the case of bromine and much more so in the case of chlorine when such values are calculated on the weight basis. Since the analytic procedure is undoubtedly most accurate for the iodine determination (the sharpest and greatest change of potential at the endpoint), and since in all the systems analysed the percentage by weight of iodine was never less than 30%, it is quite evident that the method of analysis chosen, while open to some error in the technique and procedure involved, was well suited to the accuracy requirements of this research. This is in view of the fact that considerable analytical error is needed to alter noticeably the position of any phase whose composition is plotted on the isothermal diagram.

The comparative results given in Table III indicate in general that the analytical procedure followed tends to give slightly high results. It seems probable that this error is a uniform property of all three halide determinations, since there is no noticeable change in the error for solutions of

low chlorine or of low bromine content. If the error is thus spread over the three halide values, its overall effect as far as changing the composition of the phase is concerned is negligible. There is, it is true, a noticeable tendency for the analytically determined value to be lower in cases of very high bromine or chlorine content, but this is entirely due to the difficulty of getting such a weighed halogen mixture into solution without loss through the very high vapour pressure.

On the basis of the reproducible titration results (Table II) it can be considered that such generally high results as seem to be indicated above would be due to the reduction treatment given the halogens in bringing them to the halide form. Since the values obtained, however, were sufficiently good for the purposes of this research, the above data and commentary are inserted here only because of their possible future usefulness in developing the analytical method to where it can be employed with greater accuracy.

Equilibrium determinations have shown (Table IV) that within the analytical limits previously discussed, complete solid-liquid equilibrium of this ternary system is obtained within 24 hours.

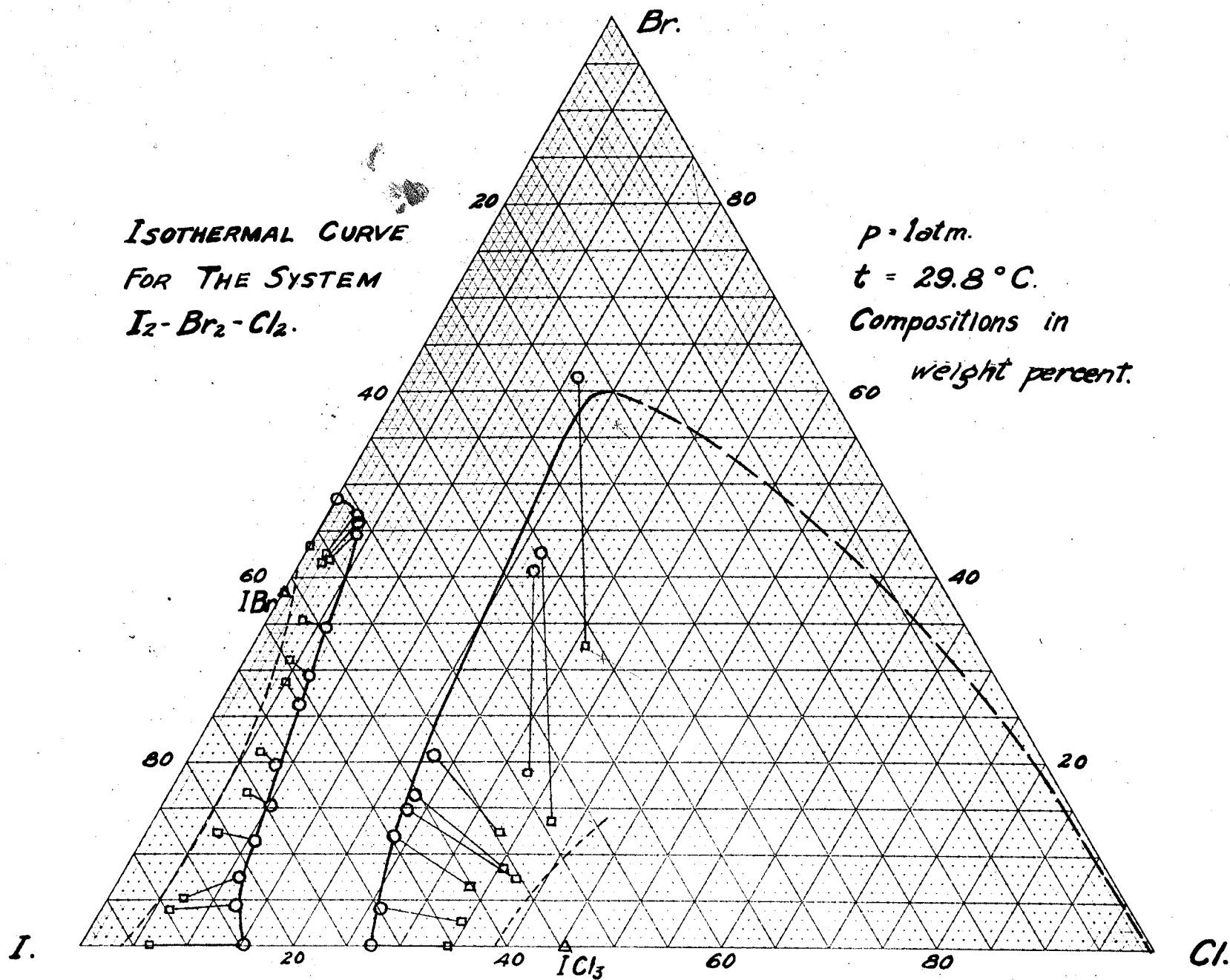
The analytical results of various solid and liquid phases have given a clear picture of the ternary system. The systems analysed fall into two groups. The first group, comprising 13 different systems, can be seen from Figure 6 to

give an excellent picture of the area of existence of the series of solid solutions ("mixed crystals") formed by IBr and solid I_2 . The solubility curve of such solid solutions in chlorine, which this first curve actually is, shows no break whatsoever. This is absolutely clear evidence that from solutions of composition within and adjacent to that area there is existent in the solid state no other compound. The fact that the solid phase separating out from such ternary systems is a series of mixed crystals of IBr and I_2 bears out, of course, the work of Terwogt⁶⁷ with the iodine-bromine system to which previous reference has been made. In comparing the results obtained in a system of I_2 and Br_2 only, careful interpolation from his data gives for $30^\circ C$ a liquid phase of 0.39 atomic per cent iodine and a solid phase of 0.43 atomic per cent iodine. In terms of weight per cent this means values for the liquid phase of 50.4% iodine, and 54.5% iodine for the solid phase.

These are in fair agreement with the values obtained in this research of 51.45% iodine for the liquid phase and 56.59% iodine for the solid phase, especially in view of the fact that Terwogt was working on a time-temperature basis and not the more accurate isothermal equilibrium determinations. Another comparison worthy of notation is to the work of Plotnikov and Rokotjan⁶⁸ who obtained the solubilities of iodine in bromine as 45% at 25° and 59.5% at $40.6^\circ C$. A linear interpolation of these to $29.8^\circ C$ gives a value of 49.8% iodine, which is again in general agreement.

At the I_2-Cl_2 end of the curve, it is found that the solubility of iodine in liquid chlorine at $29.8^\circ C$ is 84.72% iodine. The early work of Stortenbeker⁶⁹ gives a value of 87.8% iodine as the composition of the liquid phase in equilibrium with solid iodine. Here again the isothermal determination gives a much more accurate idea of the true composition of such an equilibrium phase.

While it is true that the tie-lines from liquid to solid phases in this group of systems clearly indicate the series of solid solutions from IBr to iodine, the results obtained are possibly sufficient to venture an explanation for the solid phase analysis giving a composition so far from the I-IBr line. While a good deal of the reason for this is, of course, the incomplete separation of the liquid phase from the solid phase, the appearance of the solid phase and the method of separation would leave a possible explanation resting on the crystalline isomorphism of I_2 , IBr and Cl_2 . By this is meant that it is quite conceivable, and experimental results strengthen the fact to a very limited extent, that chlorine might itself form a series of solid solutions with I_2 and IBr (i.e. Cl may dissolve in I_2 and IBr up to about 4.5%). This would tend to give a solidus line running from IBr to the I-Cl axis and somewhat closer to the I-Br axis than the points representing the composition of the solid phases of the systems examined.



On this side of the diagram there is also no evidence for the existence of IBr_2 as a solid compound at 29.8°C .

On passing to the second group of systems examined, the nine results obtained give the area of existence of the compound ICl_3 in contact with the three halogens. Due to the difficulties of obtaining a system of high bromine and chlorine content, no points beyond the line joining ICl_3 to Br_2 were obtained. However, the remainder of the curve was projected as shown by the dotted line, based on the rather doubtful figure of 99.6% iodine given by Stortenbeker⁷⁰ for equilibrium with chlorine. The other figure given by Stortenbeker for the composition of the liquid iodine and chlorine mixture in equilibrium with ICl_3 is 26.0% iodine, agreeing well with the value 27.40% obtained in this research. An interesting comparison can again be made with Plotnikov and Rokotjan⁷¹ who determined the solubility of ICl_3 in liquid Br_2 at 25°C as 70.7% ICl_3 . This is given validity by the distance from the I-Cl axis of the solubility curve for ICl_3 at 29.8°C .

The rather scattered position of the solid phase compositions is attributable in some measure to the very high vapor pressure of the solid mixtures and hence the great difficulty in a good separation and analysis. However, the possibility of a solid solution of the three halogens may again be raised, and can also be given further credence on the basis of the isomorphism of ICl_3 , Br , I_2 and Cl_2 (rhombic).

It may be finally concluded, then, that at 29.8°C there does not exist in the solid state: IBr_3 , compounds of iodine and bromine other than IBr , compounds of iodine and chlorine other than ICl_3 , or any compounds of iodine, bromine, and chlorine. A careful search of the chemical literature has also revealed no evidence to the contrary.

Since these are the results obtained, it is worth noting certain physical properties which may indicate a fundamental reason for such a conclusion.

In previous consideration of the compounds of the halogens with one another, Ephraim⁷² has stated that the central position in the molecule is occupied by the heavier, more electropositive or bulkier halogen; and that sufficient contrast must exist between these properties of the two halogens (in binary compounds) or the compound will not be formed. It would obviously follow that chlorine and fluorine could not act as the central atom, and bromine only with fluorine. Since iodine could be surrounded with a number of atoms, it is necessary to consider the possibility of intermediate compounds with iodine as the central atom. While IBr_3 has never been found to exist in the solid state, and indeed the IBr_3 group is not contained in any known polyhalogenide group,⁷³ it is clear that compounds intermediate to IBr_3 and ICl_3 might exist. Such compounds would be formulated as IClBr_2 and ICl_2Br , both having the trivalent positive iodine atom. There are, then, two major considerations to be examined:

1. Electronic Structure

The binary halogen compounds that have been examined thermally may be listed as: IF_5 , ICl_3 , ICl , IBr , BrF_3 . The compounds with iodine decrease in stability, while the combination of iodine with three atoms of chlorine, for example, can still not be explained very satisfactorily by the electron theory. Sugden's⁷⁴ use of single linkages suggests such compounds would be more stable when the two elements differ markedly in their electron affinity. This is definitely in line with their known properties, and also with determinations of their electron affinity (given by Meyer and Helmholtz⁷⁵ as $F = 95.3$, $\text{Cl} = 86.5$, $\text{Br} = 81.5$, and $\text{I} = 74.2$ Cal.). The assumption can then be made that from the point of view of existence in the solid state (i.e. thermally determinable) ICl_3 is the limiting compound (since ICl_2Br , IClBr_2 and IBr_3 have been shown not exist at 29.8°C). Quantitatively there seems to be some ground for this when the univalent crystal radii of ions are considered. The approximate values calculated by Pauling⁷⁶ are: $F = 1.36$, $\text{Cl} = 1.81$, $\text{Br} = 1.95$, $\text{I} = 2.16$. By arithmetical comparison it is then seen that, considering the negative ions, the sum obtained for $\text{Br}_3 > \text{Br}_2\text{Cl} > \text{BrCl}_2 > \text{Cl}_3$.

One other factor which also lends some weight in this direction involves a consideration of the electrons in the energy levels of the atoms under consideration. The simplest way of configuration is usually given as $F = 2.7$, $\text{Cl} = 2.8.7$, $\text{Br} = 2.8.18.7$, $\text{I} = 2.8.18.18.7$. Since there is a relatively

greater "leap" from chlorine to bromine than between any other pair, this would tend to support the assumption made above. In any attempt at theoretical substantiation of such intermediate compounds of the halogens as mentioned above, attention should be drawn to some of the pertinent information about the polyhalides. Sugden's⁷⁷ studies on higher halides enabled him to fashion rules by which he could account quite simply for all the higher halides (singlet linkages). While the halogens show considerable tendency to form polar linkages because only one electron needs to be transferred, Sugden still refuted Langmuir's⁷⁸ claim that the higher halides could be formulated as polar compounds. He did this on the basis of their properties, and then proceeded to vindicate his singlet link on the basis that stability depends more on the nature of the atom than on the nature of the link. It is also claimed by Meyer⁷⁹ that polyhalides are formed more easily and are more stable the greater the atomic weight of the halogens and the atomic volume of the cations.

If it was at all possible for a halogen to be the cation, it would be most likely iodine. However, it can feasibly be postulated that the positive metal cation as found in the known polyhalides would not be replaced by the positive iodine ion (with an atomic volume of 23.70 according to Richards⁴) to give a ternary halogen compound in the solid state. An interesting sidelight is provided by the claim made that the arguments for the existence of a positive I-ion in aqueous solution are invalid.⁸⁰

One further point may be made from the discussion by Pauling⁸¹ on the electronegativities of the elements, whence it is shown why the bond between iodine and bromine is much weaker than that between iodine and chlorine: the heat of formation from the gaseous elements of gaseous IBr is 1.7 kilocalories per mole, which is much less than the 4.0 kilocalories per mole for ICl . It has also been stated by Pauling⁸² that "The existence of ICl_3 shows that the energy of the ICl bond is enough to stabilize this molecule, even though it involves a group of five electron pairs around the iodine atom. On the other hand we might well expect that the smaller energy of the I-Br bond would not be sufficient to stabilize the molecule IBr_3 , or the intermediate compounds ICl_2Br , IClBr_2 ."

2. Molecular Volume

The fact that intermediate compounds of the type IBrCl_2 and IBr_2Cl were found not to exist in the solid state, and the fact that the maximum valency of iodine in the fluoride is 5, in chloride 3, and in bromide 1, seem to have some connection in terms of the iodine atom being unable to form such compounds, i.e. the bromine atom might be said to be saturating all the available valency of iodine.

This has some verification from the point of view of atomic volume if the iodine atom is considered to hold the central position and to be able to "hold" certain numbers of other atoms depending on their "bulk" or volume.

The atomic volumes for the elements concerned are:

$$I_2 = 24.5 (-273^\circ) \quad (\text{Sapper and Biltz})^{83}$$

$$Br_2 = 19.3 (-253^\circ) \quad (\text{W. Heuse})^{85}$$

$$Cl_2 = 16.17 (-273^\circ) \quad (\text{W. Herz})^{84}$$

On the basis of Kopp's⁸⁶ Law that for solid compounds, the sum of the atomic volumes of its constituents is approximately equal to the molecular volume of the compound, we have:

$$\begin{aligned} IBr &= 43.8 \\ ICl &= 40.7 \\ ICl_3 &= 73.0 \\ ICl_2Br &= 76.1 \\ IClBr_2 &= 79.3 \\ IBr_3 &= 82.4. \end{aligned}$$

These figures, calculated for approximately absolute zero, agree well in a relative manner with those calculated from the densities of the compound. For example:

$$\begin{aligned} IBr. \quad d &= 3.789 \text{ (I.C.T.)} \\ \text{atomic vol.} &= \frac{206.85}{3.789} = 54.6 \quad (25^\circ) \\ ICl. \quad d &= 3.1094 \text{ (Guye and Baud)}^{87} \\ \text{atomic vol.} &= \frac{162.39}{3.1094} = 53.44 \quad (25^\circ) \\ d &= 3.88 (-273^\circ) \\ \text{atomic vol.} &= 41.86. \end{aligned}$$

From the above calculations it is thus evident that the assumption of ICl_3 as a limiting point in the formation of compounds would assist in reasonably explaining why the intermediate compounds were not found in a ternary system of liquid-solid equilibrium.

C O N C L U S I O N S

The ternary system, iodine-bromine-chlorine, has been investigated isothermally at 29.8°C and the diagram for solid-liquid equilibrium obtained.

(1) No ternary compounds were found to exist in the solid state at 29.8°C.

(2) The area of existence of the compound ICl_3 has been determined for all ternary systems of composition to the left of the Br-ICl_3 line, and has been conjectured for remaining systems at 29.8°C.

(3) The area of existence of solid solutions of IBr and I_2 has been determined completely in the ternary system at 29.8°C.

(4) Certain theoretical considerations have been advanced in an attempt to explain the non-existence in the solid state of such ternary compounds as IBrCl_2 and IBr_2Cl .

(5) A method of electrometric volumetric analysis for chlorine, bromine and iodine has been successfully applied to neutral solutions of the sodium salts.

ACKNOWLEDGMENT

The author wishes to express his sincere thanks and appreciation to Dr. A.N. Campbell for his original suggestion of the problem, and for his most helpful advice and unfailing kindness in the supervision of the resultant investigation and research.

B I B L I O G R A P H Y

The following bibliography is an attempt to cover the field of research in equilibrium systems of pairs of the three halogens: iodine, bromine, and iodine. While there may be certain omissions, I believe the list is reasonably complete. There is included, also, certain references to theoretical considerations involved in such research. There is, however, but little mention made of the polyhalides; and no attempt has been made to deal with methods of analysis of the halides.

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