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EQUILIBRIUM IN THE REACTION OF BARIUM WITH CALCIUM CHLORIDE

by

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I. INTRODUCTION

Reactions of metals and fused salts are of interest for several reasons. A number of metals are prepared by metallothermic reduction of the metal oxide or halide by a more active metal. The free energy of the reaction governs the completeness of the reaction while from the enthalpy of the reaction an estimate of the adiabatic temperature rise may be calculated. The solubility of the reductant in the fused bath will affect the excess active metal needed and the solubility of the molten salt in the product will affect the purity of the product. In the preparation of metals by electrolysis of a fused salt, the free energy of formation of the metal salt gives the minimum voltage at which the electrolysis cell can operate. The solubility of the metal in the electrolyte is a major factor governing the current efficiency of the cell while the solubility of the electrolyte in the metal will affect the purity of the product.

It is possible to obtain thermodynamic data from a study of the reactions of metals with fused salts. For a reaction such as:

$$A + BC \rightleftharpoons B + AC \qquad \text{(equation 1),}$$

the equilibrium constant may be written as:

$$K = \frac{A_B \times A_{AC}}{A_A \times A_{BC}} \qquad \text{(equation 2)}$$

where A_i is the activity of substance i. Since at equilibrium the activity of a substance is equal in all coexisting phases, the activity of any substance may be measured or estimated in any of the phases. The standard free energy of the reaction is given by:

$$\Delta F^\circ = - RT \ln K \qquad \text{(equation 3)}$$

and the standard enthalpy of the reaction is given by:

$$\frac{d \ln K}{d T} = \frac{\Delta H^\circ}{RT^2} \qquad \text{(equation 4).}$$

Since ΔH° is often approximately constant over a short temperature range, equation 4 may be integrated and rearranged to give:

$$\Delta H^\circ = \frac{-RT_1 T_2 \ln \frac{K(T_2)}{K(T_1)}}{T_1 - T_2} \qquad \text{(equation 5).}$$

By determining the equilibrium constant at two different temperatures, the enthalpy of the reaction may be evaluated. If the metals A and B form an ideal solution and the salts BC and AC also form an ideal solution and there is a negligible amount of metal dissolved in the salt and of salt dissolved in the metal, the activities may be replaced by mole fractions. The equilibrium will obey the ideal law of mass action and the equilibrium constant may be written as:

$$K = \frac{N_B \times N_{AC}}{N_A \times N_{BC}} \qquad \text{(equation 6)}$$

where N_A and N_B are the mole fractions of A and B in the metal phase and N_{AC} and N_{BC} are the mole fractions of AC and BC in the salt phase.

If there is an appreciable amount of metal dissolved in the salt or of salt dissolved in the metal, it is not possible to determine the concentrations of the individual chemical species in solution by chemical analysis. Only the total amount of A, B, and C in each phase can be determined. It is necessary to make an assumption in order to be able to calculate concentrations of the individual species as required for equation 6. The nature of the dissolved entity in solutions of a metal in a liquid halide salt is not definitely known. Excess metal atoms in solid ionic crystals have been studied extensively and many of their properties measured. These solid solutions are considered to consist of a normal cation lattice and an anion lattice containing vacancies which are occupied by the electrons from the excess metal. In this picture, the metal atom is separated into electrons and a metal ion in the solution process. Subsequently, the electron is not associated with any single metal ion. The extension of this concept to liquid salt solutions would seem to be reasonable. For a liquid salt consisting of two kinds of cations, the model becomes somewhat complex. To treat such a solution as being composed of a melt of two metal halides with a certain amount of each metal in solution implies that these four chemical species are distinguishable. Even through these species may not be distinguishable on an atomistic model, the postulatution may be useful in a thermodynamic description of the system.

Instead of using the ideal law of mass action, van Laar and Lorenz (1) proposed an equilibrium law based on the use of van der Waal's equation to account for the concentration dependence of the activity coefficients in the metal and salt phases. This law contained two adjustable parameters which were related to the interaction forces between the several chemical species and which were evaluated, with the equilibrium constant, from values of the concentration quotient at three different concentrations. The law was applied to his data on the reaction of cadmium with lead chloride and of lead with stannous chloride. These reactions were carried out in glass tubes and cooled by an air quench. The equilibrium constant did not agree with values calculated from free energies of formation. Körber and Oelsen (2) have shown that the results of Lorenz on these systems can be explained by insufficient rapidity of the quench.

There is also interest in the nature of these solutions of metals in a fused salt. Most early workers, in particular Guntz, proposed the formation of subhalides. Guntz and Benoit (3) measured the heat of solution of a mixture of calcium and calcium chloride that had been heated to 1000°C and cooled. From these data, the heat of formation of calcium monochloride was calculated. Bichowsky and Rossini (4) have shown that the heat of solution obtained for calcium monochloride is very close to the value calculated for a mixture of calcium metal and calcium chloride. In general, the existence of subhalides of alkalies and alkaline earths has not been confirmed.

Lorenz studied a number of mixtures of metals in molten salts and proposed that the metals were colloidally dispersed in the fused salt. This work has been summarized in the book, "Pyrosole", by Lorenz and Eitel (5). Aten (6) found that cadmium lowered the melting point and decreased the specific conductivity of cadmium chloride indicating a true solution. Eitel and Lange (7) examined this molten mixture under an ultramicroscope and found no evidence for the existence of colloidal particles in the molten salt and observed no Tyndal effect.

Cubicciotti (8) found the conductivity of solutions of calcium in calcium chloride at 850°C decreased as more calcium metal was added. Heymann (9) discusses the solution of cadmium in cadmium chloride and concluded that the cadmium dissolved as a solvated form:

$$\mathrm{Cd} + x\mathrm{Cd}^{++} \rightleftharpoons \mathrm{Cd}\cdot x\mathrm{Cd}^{++}.$$

With x equal to unity, this proposal would be equivalent to a dimerized monochloride.

The simplest method of presenting data showing the equilibrium phase compositions of the metal and salt phases is as an isothermal section of a ternary phase diagram. A system composed of four chemical species which are related by a chemical reaction is a three component system. This follows from defining the number of components as the minimum number of composition terms necessary for the complete statement of the composition of all phases in the system. For a reaction such as equation 1, an equilibrium constant may be written for each phase. Then, knowing the equilibrium constant and the activity coefficients, the concentration of one substance can be calculated if the others are known. This may be generalized as:

$$c = s - r \qquad \text{(equation 7)}$$

where c is the number of components, s is the number of chemical species, and r is the number of independent reactions. This type of system is known as a reciprocal or metathetical ternary phase system. The components may be taken as A, B, and C or as any three of the four species. The diagram is most conveniently plotted as a square figure with a pure specie at each corner and either temperature or pressure on the vertical axis, the other being held constant. The sides of the diagram are the respective binary systems. For a composition-temperature diagram at constant pressure, the number of degrees of freedom (f) of the system is given by the phase rule:

$$f = c - P + 1 \qquad \text{(equation 8)}$$

where P is the number of phases in equilibrium exclusive of the vapor phase and c is the number of components. For a ternary system,

$$f = 4 - P \qquad \text{(equation 9)}$$

Rinck (10) studied the equilibrium in the reaction of potassium with sodium hydroxide, sodium flouride, sodium chloride, sodium bromide and sodium iodide. Mixtures of the metals and salts were heated in sealed capsules of iron, quenched in cold water, and the salt and metal phases analyzed. The metal which was dissolved in the salt phase was removed by leaching with alcohol in the investigation of the potassium-sodium chloride system. For the other systems, the metal dissolved in the salt phase was determined by titrating the alkalinity with standard acid. The analysis of the salt phase was corrected for this dissolved metal by assuming that the ratio of sodium metal to potassium metal in the salt was equal to that in the metal phase. The magnitude of the solubility of the metal in the molten salt was not reported. With the exception of the potassium-sodium hydroxide system, the equilibrium constants did not vary with concentration and seem to obey the ideal law of mass action. The equilibrium constants agreed closely with values calculated from the free energies of formation of the metal halides. The variation of the equilibrium constant with temperature was less than experimental error except for the potassium-sodium chloride system. Rinck fitted his data to Lorenz's equation and obtained equilibrium constants which varied with concentration and did not agree with the values calculated from the free energies of formation. As a result, Rinck concluded that these systems did not follow the equilibrium law proposed by Lorenz.

The reaction of calcium with strontium chloride has been studied by Ostertage (11). The experimental method which was used was similar to that used by Rinck (10) in studying the sodium-potassium systems. Steel capsules were used to contain the reaction mixtures and after quenching in cold water, the salt and metal phases were analyzed. The equilibrium concentration quotient and calculated standard free energy of the reaction were found to vary with composition. When plotted against the atomic percent strontium in the metal phase, the values passed through a maximum at 10 atomic percent strontium. A plot of the atomic percent calcium dissolved in the salt phase verses atomic percent strontium in the metal phase also had a maximum at the same strontium concentration. By chemical analysis, it is only possible to determine the total amount of metal dissolved in the salt phase and not the individual species, and presumably it was the total metal dissolved in the salt that was reported. No correction of the equilibrium concentration quotient for this metal dissolved in the salt phase was mentioned. The equilibrium concentration quotient rose steeply from 4×10^{-2} at one atomic percent strontium to 6.5×10^{-2} at

10 atomic percent strontium and then dropped linearly to 3×10^{-2} at 55 atomic percent strontium. The values were averaged to give a concentration quotient of $4.95 \pm 2.0 \times 10^{-2}$ as compared to 3.82×10^{-2} calculated from the free energy of formation of the metal chlorides. Ostertage suggested that the variation of the equilibrium constant was due to the heat of solution of the metal in the salt and not to the heats of mixing of the salts or the metals. This suggestion was based on the similar variation of the equilibrium concentration quotient and the solubility of metal with the composition of the salt phase.

Jellinek and Wolff (12) have investigated the reaction of barium dissolved in lead with calcium chloride. A mixture of fused calcium chloride and barium chloride was electrolyzed with a lead cathode. From the analysis of the resulting salt and metal phases, the equilibrium constant was calculated for the reaction:

$$\text{Ba in lead} + CaCl_2 \rightleftharpoons BaCl_2 + \text{Ca in lead.}$$

An equilibrium constant of 1.5 was obtained at 1000°C. The corresponding free energy change is - 1.03 k cal as compared with a value of about - 10 k cal calculated from the free energies of formation of calcium chloride and barium chloride. Some possible sources of error in this value of the equilibrium constant are as follows: (1) the assumption of ideal solution in the metal phase. Since both calcium and barium form a series of intermetallic compounds with lead, negative deviation from

Raoult's law is probable. If there is deviation for Raoult's law, the concentration quotient would be equal to the equilibrium constant only if the activity coefficient of calcium in lead is equal to the activity coefficient of barium in lead. (2) Since a current of 12 amperes was used for the electrolysis, large concentration gradients through the salt phase could have been produced. Also, polarization of the electrodes could have produced concentrations of calcium chloride and barium chloride in the immediate vicinity of the electrodes which were different from those in the bulk of the salt phase. If this was true, the salt composition in equilibrium with the metal was not the same as the composition of the salt phase found by analysis. (3) The salt and alloy mixture was not quenched and thus could change in composition as the various phases solidified. The poor agreement between the free energy of this reaction as measured by this equilibrium constant and the value calculated from other data indicates that the equilibrium constant found by Jellinek and Wolff does not apply to the calcium-barium chloride equilibrium system.

This investigation is concerned with the reaction of barium with calcium chloride. The experimental method used was similar to that used by Rinck (10) in studying the sodium-potassium systems. Stainless steel capsules were used to contain the reaction mixtures and after quenching in cold water, the salt and metal phases were analyzed.

Differential thermal analysis was used to locate the phase boundaries in the ternary system. The calcium-barium-barium chloride-calcium chloride ternary phase diagram was partially determined and isothermal sections at 900°C and 950°C are presented with some equilibrium concentration quotients. The experimental solubility of metal in the salt at various metal compositions is compared with solubilities calculated with various assumptions as to the solubility law governing this solubility.

II. EXPERIMENTAL

A. Materials

1. Calcium chloride

Calcium chloride was prepared by dehydrating Bakers analyzed hydrated calcium chloride. The dehydration was carried out by first heating the salt from 60° to 140°C in air over a period of about two days in a glass vessel. The calcium chloride was then transferred to a platinum boat and fused under dry hydrogen chloride by heating to 850°C over a period of about 8 to 10 hours. The dry hydrogen chloride was prepared by mixing concentrated hydrochloric and sulfuric acids and was further purified by bubbling through a flask containing glass beads and concentrated sulfuric acid. The anhydrous calcium chloride was stored in a screw top bottle in a dry box. The hydrated calcium chloride was reported to be 99.95 percent pure. After dehydration, it contained less than 0.01 percent platinum from the platinum boat and from 0 to 0.006 percent calcium oxide as determined by titration with standard hydrochloric acid. The pure anhydrous calcium chloride melted at 770°C. A sample of calcium chloride which contained a small amount of water melted at 773°C. These values are compared with values reported by other investigators in Table 1. The liquid calcium chloride supercooled as much as 60°C during the cooling portion of the thermal analysis. However, after crystallization was initiated, the temperature increased to a constant value which was taken as the melting point. The same value for the melting point was obtained on both melting and freezing. Seeding the melt with crystals of calcium chloride or stirring to minimize supercooling was impractical since the thermal analysis capsules were sealed.

Table 1. Melting point of calcium chloride

Investigator	Melting point
This investigation	770[a]
This investigation	773[b]
Neumann, et al. (13)	771
Sandonnini (14)	772
Schaefer, W. (15)	773
Bukhalova and Bergman (16)	773
Eastman, et al. (17)	773
Sato and Amano (18)	777
Ferrari and Inganni (19)	780
Moore (20)	782[c]

[a] Pure anhydrous calcium chloride.

[b] Calcium chloride containing a small amount of water.

[c] Reported for calcium chloride containing 0.6 percent magnesium chloride.

Table 2. Melting point and α - β transformation temperature of barium chloride

Investigator	Transformation	Melting point
This investigation	926	962
Ruff and Plato (21)		960
Winter (22)	920	962
Schaefer, W. (15)		960
Sato (23)	927	963
Sandonnini (14)	923	960
Bukhulova and Bergman (16)		962
Eastman, et al. (17)	920	960

2. Barium chloride

Anhydrous barium chloride was prepared by dehydrating Baker's analyzed hydrated barium chloride. The hydrated salt was heated from 60°C to 140°C over a period of about two days in air. It was then partially fused by heating in a platinum boat to between 950°C and 1000°C in an atmosphere of dry hydrogen chloride. The anhydrous barium chloride was stored in a screw top bottle in the dry box. The hydrated salt was reported to be about 99.85 percent barium chloride and contained about 0.1 percent total calcium and strontium. The final product was neutral to phenolphthalein and probably contained about 0.01 percent platinum from the platinum boat. The anhydrous barium chloride melted at 962°C and the α - β transformation occurred at 926°C. These values are compared with values reported by other investigators in Table 2. The agreement in this case is very good.

3. Calcium metal

Calcium metal, which had been prepared by the aluminothermic reduction of calcium oxide, was obtained from the New England Lime Co., Canaan, Connecticut, and was distilled under vacuum using the method described by Smith, et al. (24). The redistilled calcium contained about 0.002 percent aluminum, 0.005 percent iron, 0.005 percent nitrogen, 0.003 percent manganese, and 0.03 percent magnesium. Smith, et al., (24) estimated the oxygen content of this type calcium to be less than 0.01 percent on the basis of the nitrogen analysis. This calcium was obtained as rough lumps of massive metal about $1\frac{1}{2}$ inches in diameter. These pieces were cut in air to the proper size for charging into the capsules and the surfaces cleaned with a file in a dry box filled with argon. This calcium melted at 836°C. This value is compared with values reported by other investigators in Table 3.

4. Barium metal

Impure cast barium sticks were purified by double distillation under reduced pressure. The distillation retort was a closed end

Table 3. Melting point of calcium metal

Investigator	Melting point
This investigation	836
Hartmann and May (25)	810
Eastman, et al. (17)	828
Kubaschewski (26)	830
Sheldon (27)	840
Rinck (10)	848
Antropoff and Falk (28)	851[a]
Hoffmann and Schulze (29)	851[b]

[a] These investigators found 848° but estimated the melting point of nitrogen free calcium metal to be 851°.

[b] These investigators found 849° but following the example of Antropoff and Falk (28) estimated 851°.

cylinder of type 304 stainless steel. An air cooled cold finger condenser was bolted to the retort flange and was sealed with a rubber O-ring gasket. The retort had an inside diameter of 4 3/4 inches and was 18 inches long. About 10 inches of the retort extended into a modified Lindberg type CR-5 resistance furnace. The cold finger had an outside diameter of 3½ inches and was 12 inches long. The crude barium was placed in four trays made of type 405 stainless steel. These trays were one inch deep and stacked one on top of another in the retort. The top three trays had a two inch diameter hole in the center to permit barium vapor to flow up to the cold finger. A ½ inch

Table 4. Barium metal analysis

	Nitrogen ppm.	Carbon ppm.	Iron ppm.	Manganese ppm.
Crude barium	430	500-800	53	50
Single distilled barium	73	35	23	80

rim around the hole prevented the molten barium from running out of the tray. The retort was loaded with about 700 grams of barium and heated to 500°C under a pressure of 25 microns of mercury. The system was filled with argon to a pressure of about 4 millimeters of mercury and was heated to about 900°C for 8 to 10 hours. The temperature of the cold finger was about 200°C. After distillation, the retort was placed in an argon filled dry box and the barium crystals were removed from the cold finger with a chisel. The metal was placed in a screw top bottle and was stored in a dry box. The distilled barium was obtained as needlelike crystals about 2 millimeters in diameter and from 10 to 30 millimeters long. A residue of metal covered with a crust of crystalline barium oxide was left in the trays. A mixture of the crust and metal residue contained about 0.15 percent nitrogen. The analysis of the crude and single distilled barium is given in Table 4.

Table 5. Melting point of barium metal

Investigator	Melting point
This investigation	717[a]
This investigation	729[b]
Hartman and May (25)	658
Hoffman and Schulze (29)	704
Rinck (10)	710
Hirst, et al. (30)	714
Eastman, et al. (17)	717
Guntz (31)	850

[a] Crude barium.

[b] Double distilled barium.

From these analyses and from qualitative spectrographic analyses, the total amount of silicon, magnesium, nickel, copper, aluminum, strontium, and calcium was estimated to be less than 160 parts per million. No oxygen or hydrogen analyses were available. Excluding oxygen and hydrogen, the metal would be about 99.96 percent pure barium metal. The crude barium melted at 717°C and the double distilled barium melted at 729°C. These values are compared with values reported by other investigators in Table 5. A sample of the double distilled barium metal to which was added 0.175 weight percent oxygen or 1.5 mole percent barium oxide melted between 650° and 613°C with the liquidus occurring at 650°C and a eutectic type thermal arrest occurring at 613°C. Assuming that the liquidus is approximately linear in the region of pure barium, this corresponds to a lowering of 45.7°C per 0.1 weight percent oxygen. An oxygen impurity of 0.044 percent would thus lower the melting point of barium metal to about 710°C which is the usually accepted value.

B. Methods

1. Isothermal tie-lines

a. Apparatus The tie-lines of the isothermal sections at 900°C and 950°C were determined by equilibrating mixtures of the metals and salts at the operating temperature and quenching in cold water. The starting materials were mixtures of either calcium metal and barium chloride or barium metal and calcium chloride. The containers for these samples were made of type 304 stainless steel and are illustrated in Figure 1. The capsules were made from six inch sections of 7/16 inside diameter seamless tubing with a 0.035 inch wall. These pieces of tubing were pickeled in a 50-50 mixture of concentrated nitric and hydrochloric acids, washed with distilled water and dried at 140°C. One end of the tube was pinched flat and welded shut with an electric arc in a dry box filled with argon. After

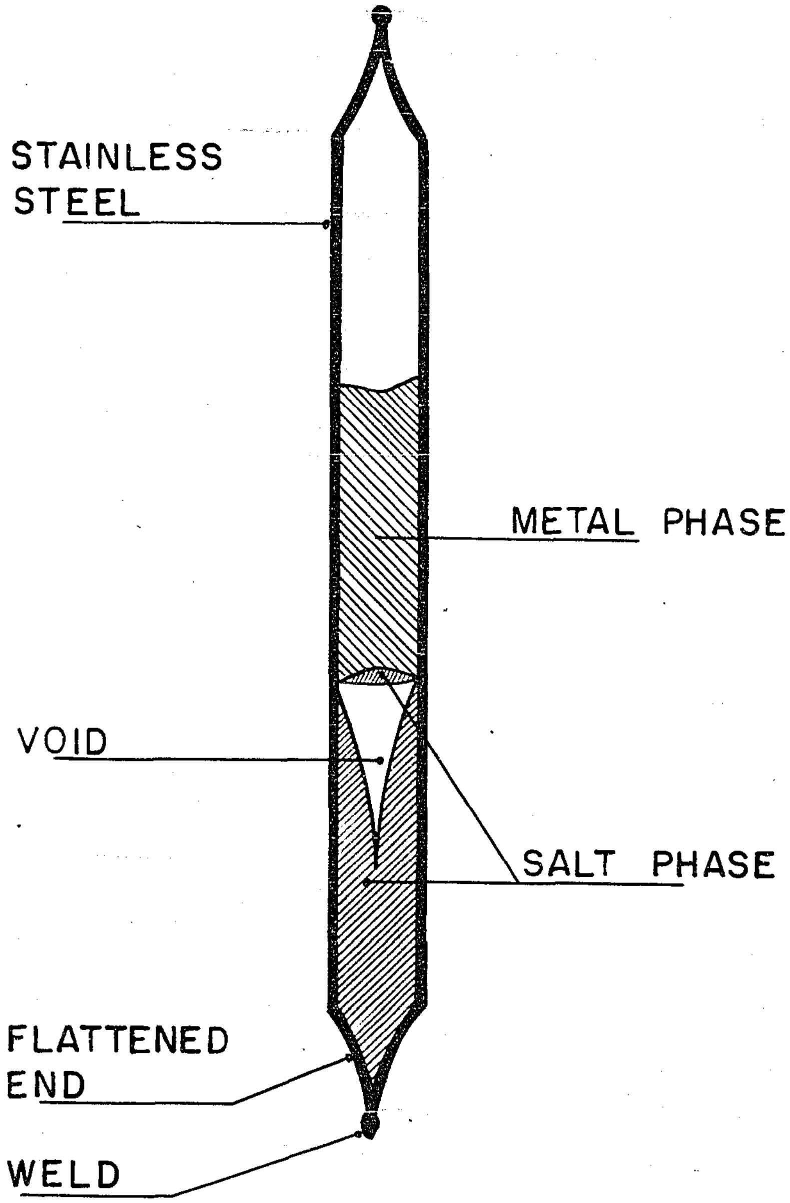

Figure 1. Sample capsule

the capsules were filled in the dry box, the other end was pinched flat and sealed by welding in the dry box. All weighing and loading operations were carried out in a dry box which was about 24 inches by 12 inches by 6 inches high. This dry box could be evacuated to between 20 and 30 microns of mercury and filled with argon. Linde argon, reported to be 99.99 percent pure, was used for filling the dry box except when barium metal was used as one of the starting materials. In this case, the argon was purified by passage over granular calcium at 450°C. The barium metal slowly discolored even after these precautions were taken. The apparatus for equilibrating the samples is shown in Figure 2. A Hoskins Type FH303A resistance furnace was used to heat the sample capsules. It was mounted on a frame so that it could be rotated through 180° to facilitate mixing of the two phases. One end of the furnace was closed with a three inch plug of K-30 fire brick. The other end was closed with a plug made from a fused silica tube which was three inches long and had an outside diameter of 1 5/16 inches and a 5/16 inch wall. A thermocouple tube extended through the fused silica tube and the silica tube was filled with Sauereisen no. 1500 refractory cement. The hot side of this cement was protected with an asbestos plug. A chromel-alumel thermocouple was used to measure the temperature. The sample capsule was wired to the thermocouple and could be removed from the furnace for quenching by using

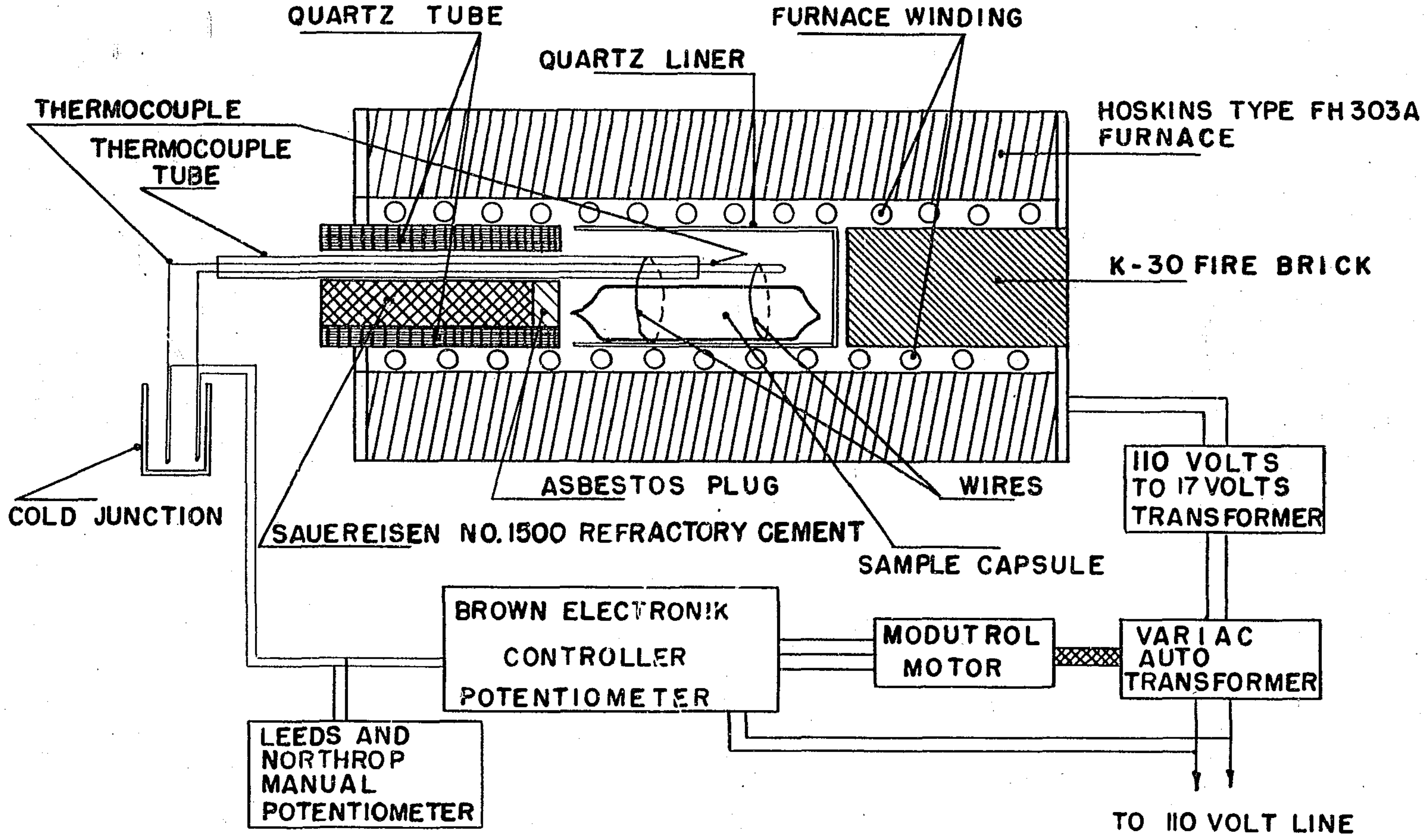

Figure 2. Schematic drawing of sample furnace

the thermocouple tube as a handle. The temperature of the furnace was controlled with a Brown Electronik circular scale recording potentiometer which actuated a Modutrol motor coupled to a Variac auto transformer. The temperature was constant within the furnace cavity to about ± 3°C. The sample temperature was also measured with a Leeds and Northrop no. 8657C manual potentiometer.

b. Operating procedure The materials charged into the equilibration tubes were carefully weighed so that the desired composition would be obtained. Samples of metal and salt were first weighed to 0.1 gram on a beam balance in the dry box and placed in screw top bottles. The bottles were removed from the dry box and weighed on an analytical balance to 0.1 milligram. The bottles were replaced in the dry box which was again evacuated and filled with argon. The metal and salt charges were transferred to the stainless steel capsules. The bottles were reweighed and the weight of the sample components obtained by difference.

The capsules were welded shut, placed in the furance, and heated for about 3 hours. The furnace was rotated through 180° and shaken to mix the phases at intervals during the first two hours. The capsules were held in a vertical position for the last hour to permit phase separation. Some samples at 900°C were heated for 12 hours to determine whether equilibrium had been reached. The variation in the analysis of the phases between the samples heated for 12 hours and those heated for 3 hours was less than the experimental error in the analytical methods. After the heating period, the capsules were removed from the furnace and quenched in cold water. The time required to transfer the samples from the furnace to the water was about 2 seconds.

The stainless steel capsules were slotted on opposite sides with a dry silicon carbide cut-off wheel, the two ends of the capsules were cut off with a hack saw, and the capsules were loaded into the dry box. After the dry box was evacuated and filled with argon, the stainless steel capsule was peeled away with vise grip pliers and the salt and metal phases were separated and sampled. The salt phase varied in color from light brown to black and had a hollow solidification pipe extending down through the center. In some runs at 950°C, a small metal bead was found in the pipe which indicated that some phase separation occurred during the quench. Figure 1 shows the arrangement of the phases in a quenched capsule. In binary samples of barium metal and barium chloride, the positions of the metal and salt phases were reversed.

The samples run at 900°C were divided into individual portions for the various analyses and placed in small screw top bottles for weighing. Due to the apparent separation of metal from the salt phase on quenching samples from 950°C, as much of each phase as could be recovered was taken as the sample, dissolved in a volumetric flask, and aliquots were taken for the individual analyses.

c. Analysis The amount of metal dissolved in the salt phase was determined by dissolving a sample in distilled water and titrating with standard one tenth normal hydrochloric acid using phenolphthalein or methyl red as the indicator. The amount of chloride in the salt was determined gravimetricly by precipitating and weighing as silver chloride. The amount of calcium in the salt phase was calculated with the following equation derived from a material balance (see Appendix A):

$$\% \text{ Ca} = \frac{\dfrac{\% \text{ Cl}^-}{70.914} + M_M - \dfrac{100 - \% \text{ Cl}}{137.36}}{0.01767} \qquad \text{(equation 10)}$$

where M_M was the moles of metal dissolved in 100 grams of sample. Barium was determined by difference. This method of analysis was used instead of analyzing directly for calcium and barium because the chloride analysis and base titration can be done with high precision and because of the difficulty of separating mixtures of calcium and barium over a wide concentration range.

The amount of chloride in the metal phase was determined gravimetricly by precipitating and weighing as silver chloride. The amount of calcium and barium in the metal phase was determined by precipitating calcium and barium sulfate in water with sulfuric acid and diluting with absolute methanol to a final concentration of 90 percent methanol by volume. The amount of calcium could then be calculated with the following equation (see Appendix B):

$$\% \text{ Ca} = \frac{\text{wt. } MSO_4 - 1.6993(100 - \% \text{ Cl})}{1.6974} \qquad \text{(equation 11)}$$

where wt. MSO_4 was the weight of calcium and barium sulfates which would have been produced by a 100 gram sample of metal. Barium was determined by difference. By using this method, the calcium and barium did not have to be separated.

The amount of calcium and barium was also determined by using equations derived from a material balance between the initial overall composition and the salt phase composition (see Appendix C). These equations are as follows:

$$\% \text{ Ca} = \frac{N_{Ca} \times 40.08 \times \% \text{ Cl}^-}{N_{MCl_2} \times 70.914} \qquad \text{(equation 12)}$$

$$\% \text{ Ba} = \frac{N_{Ba} \times 137.36 \times \% \text{ Cl}^-}{N_{MCl_2} \times 70.914} \qquad \text{(equation 13)}$$

The sulfate method gave results which were consistently higher in barium than the material balance method and the difference in the two methods was independent of the starting materials. The primary source of error in the material balance method was in transferring the weighed salt into the capsule. This error would change direction when calcium chloride was used in the charge rather than barium chloride and this change was not observed. Also, in the sulfate method, samples containing only barium metal and barium chloride gave a total analysis of about 100 percent while samples containing only calcium metal and calcium chloride gave a total analysis varying from 95 to 98 percent. This error may be due to coprecipitation of calcium chloride with the calcium sulfate. For these reasons, the material balance method is considered to be the most accurate.

2. Thermal analysis

Phase boundaries in the ternary and the binary systems were located by differential thermal analysis. Thermal analyses were performed on samples contained in capsules made from 2½ inch lengths of Type 304 stainless steel tubing. A stainless steel cap containing a thermocouple well was welded on the top of the tube. A sectional view of this type of capsule is shown in Figure 3. The charge components were weighed in the same manner as the starting materials for the determination of the isothermal sections. The capsules would hold about 30 grams of barium chloride, 20 grams of of calcium chloride, 17 grams of barium metal, or 13 grams of

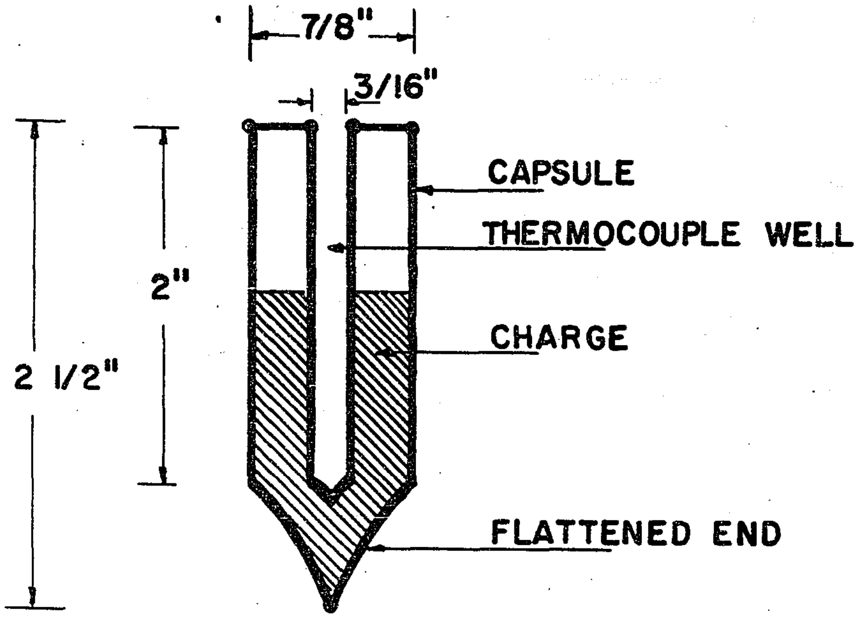

Figure 3. Thermal analysis capsule

calcium metal. After the capsule was charged in the dry box, the bottom of the capsule was pinched flat and sealed by welding in the dry box.

The charged capsule was placed in the thermal analysis apparatus shown in Figure 4. A Hoskins Type FHS304 resistance tube furnace was used to heat the samples. The furnace was closed at each end with a six inch long plug of K-30 fire brick. A $\frac{1}{4}$ inch diameter hole was drilled in the center of the top plug to permit insertion of the sample thermocouple. Two concentric quartz liners were placed in the center of the furnace surrounding the sample capsule. The differential thermocouple was placed between these two liners and measured the furnace temperature. The leads of this thermocouple were brought out of the furnace between the bottom fire brick and the furnace liner. The cold junctions of these thermocouples were placed in glass tubes containing mercury in an ice bath. The E.M.F. from the sample thermocouple was recorded by the X_1 channel of a Leeds and Northrop Speedomax Type G X_1 - X_2 recording potentiometer. The sample temperature was checked at all critical points with a Leeds and Northrop No. 8657-C manual potentiometer. The negative lead of the differential thermocouple was connected to the negative lead of the sample thermocouple. The E.M.F. between the differential thermocouple positive lead and the sample thermocouple positive lead was

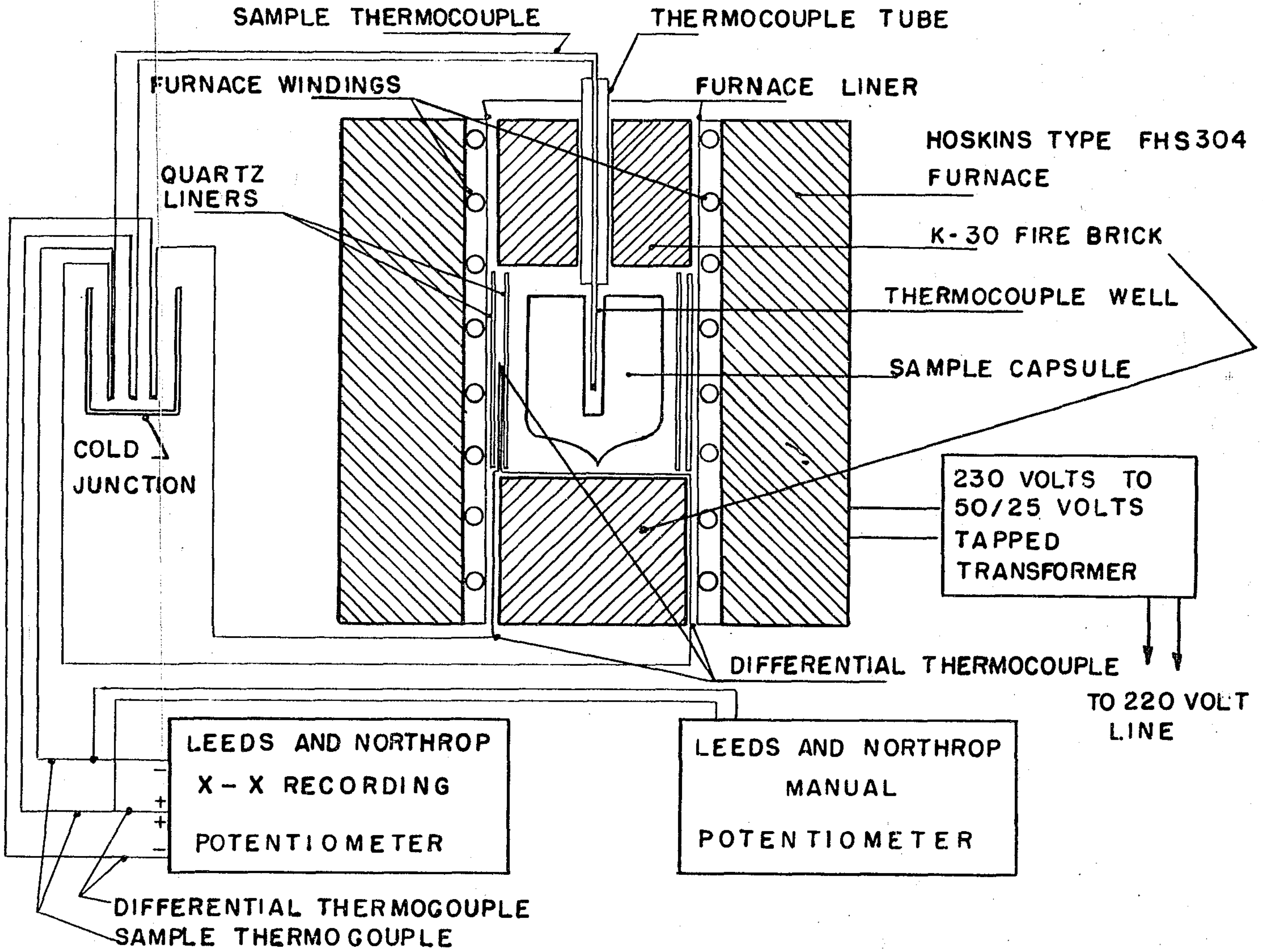

Figure 4. Schematic drawing of thermal analysis furnace

recorded by the X_2 channel of the Leeds and Northrop recorder. With this arrangement, the X_2 recorder measured the difference in temperature between the furnace and the sample and was a very sensitive means for detecting thermal effects. The thermocouples were made from 22 gauge chromel and alumel thermocouple wire. The sample thermocouple was standardized against a U. S. Bureau of Standards standard melting point aluminum sample and against a sample of coulometer grade silver. Graphite crucibles were used for the melting point standards. The crucibles were of the design recommended by the Bureau of Standards and reported by Roeser and Wensel (32) except that a quartz thermocouple protection tube surrounded by a graphite tube was used instead of a glazed porcelain tube. Spectrographic analysis showed that no silicon was picked up by the aluminum during the standardization procedure. The thermocouple agreed within 0.5°C at both of these temperatures with the table for chromel-alumel thermocouples in the National Bureau of Standards Circular 561.

III. RESULTS AND DISCUSSION

A. Binary Systems

1. Calcium-barium system

The high temperature portion of the calcium-barium system consists of a continuous series of solid solutions and has a minimum melting point at 605°C and 49 mole percent barium. The phase diagram as determined by Sheldon (27) is shown in Figure 5. No additional work was done on this system to check the reported results.

2. Calcium-calcium chloride system

The calcium-calcium chloride system contains a liquid immiscibility gap and is shown in Figure 6. The monotectic occurs at about 99.5 atomic percent calcium and 820°C. The eutectic occurs at about 2 atomic percent calcium and 768°C. The eutectic and monotectic temperatures were determined by thermal analysis while the boundaries of the liquid immiscibility gap were determined by both thermal analysis and chemical analysis of quenched samples. The agreement between the two methods was excellent. The samples quenched from 900°C gave a value of 3.8 mole percent for the solubility of calcium in calcium chloride and 1.02 mole percent for the solubility of calcium

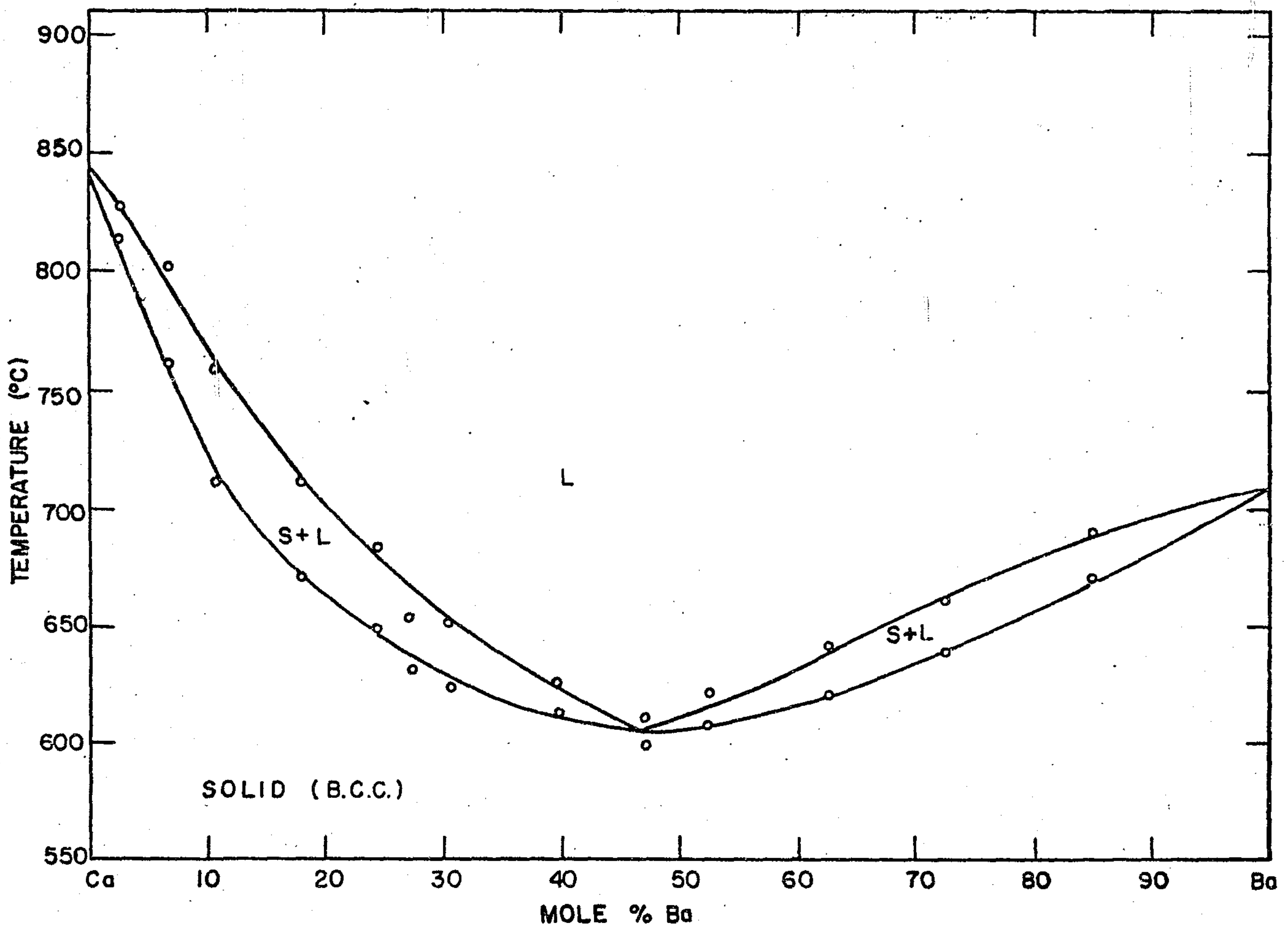

Figure 5. Calcium-barium phase diagram

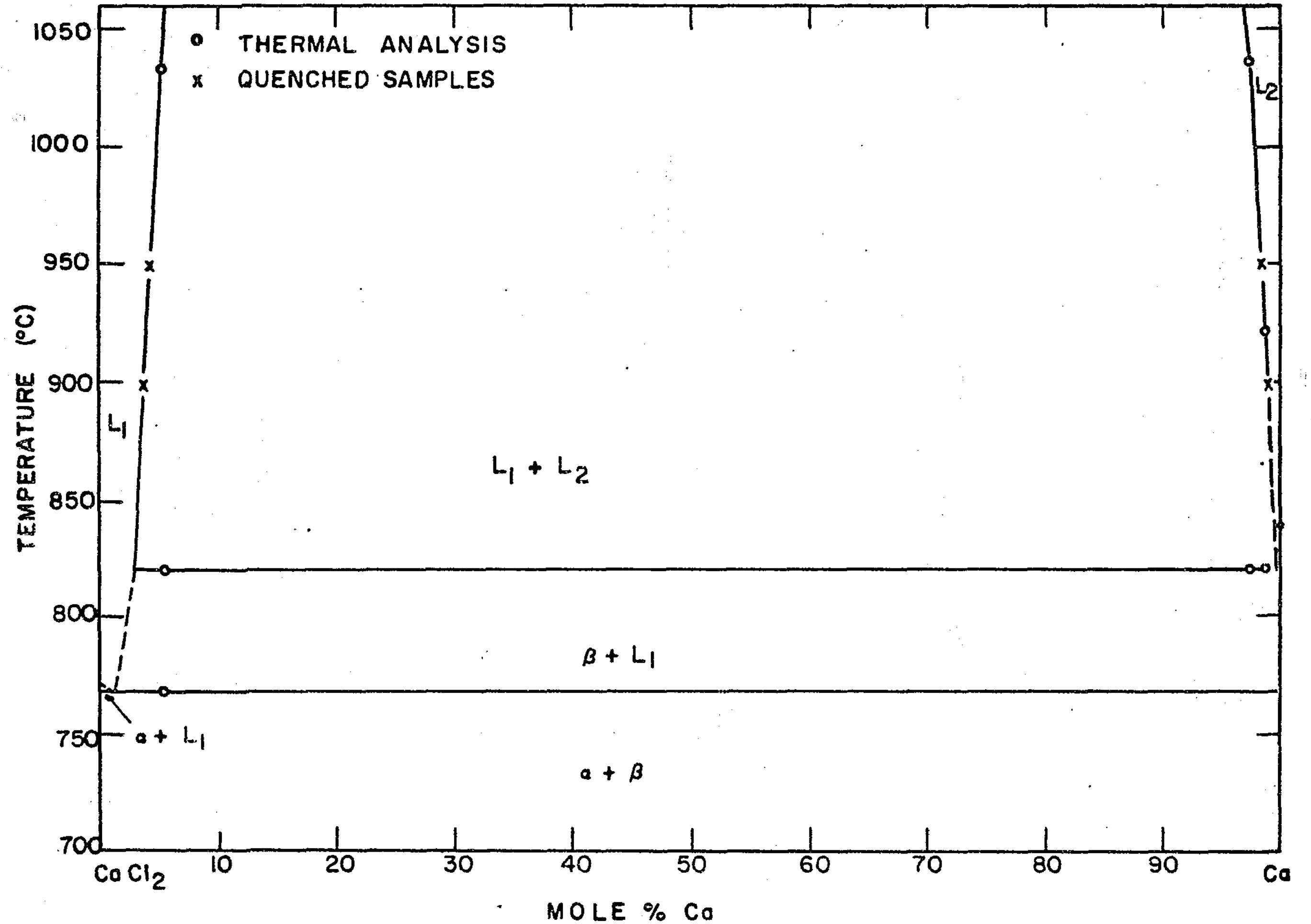

Figure 6. Calcium-calcium chloride phase diagram

chloride in calcium metal. A sample of calcium chloride which contained a small amount of water gave about 20 mole percent calcium metal dissolved in calcium chloride due to the formation of calcium hydride and calcium oxide or hydroxide. The sample quenched from 950°C gave a value of 4.2 mole percent for the solubility of calcium in calcium chloride and 1.56 mole percent for the solubility of calcium chloride in calcium metal.

Samples of calcium chloride containing 5.37, 97.4 and 98.8 mole percent calcium metal were used for thermal analysis. The eutectic halt was well defined on both heating and cooling curves for 5.37 percent sample. This sample supercooled about 25°C but after crystallization was initiated the temperature rose to a constant value of 768°C. The eutectic break was not detectable on the 97.4 and 98.8 percent calcium samples. This was probably due to small amount of salt present and to supercooling. The thermal effects due to the liquid immiscibility gap were only observed on the time-temperature differential cooling curves. This break was well defined for the sample containing 5.37 percent calcium but was barely discernible for the samples containing 97.4 and 98.8 percent calcium. The cooling curve data are summarized in Table 6. This diagram is in good agreement with the eutectic and monotectic temperatures, i.e., 767°C and 825°C respectively reported by Eastman, et al., (17). The calcium side of

Table 6. Thermal analysis of calcium-calcium chloride

Composition mole % Ca	Immiscibility gap boundary °C	Monotectic horizontal °C	Eutectic horizontal °C
5.37	1033	820	768
97.4	1035	820	
98.8	921	820	

the immiscibility gap is also in good agreement with these authors. The solubility of solid and liquid calcium in liquid calcium chloride is in marked disagreement. The monotectic salt composition reported by Eastman, et al. (17), was 20 mole percent calcium as opposed to about 3 mole percent calcium found in this investigation. The reported solubility then decreased to 15 mole percent calcium at 950°C and increased to 30 mole percent calcium at 1200°C. This large solubility was possibly due to water or oxide contamination of the calcium or calcium chloride. Bredig, et al., (33) reported a value of 6.15 mole percent calcium metal dissolved in calcium chloride as determined by hydrogen evolution and 9.75 mole percent calcium metal dissolved in calcium chloride as determined by hydroxide titration. These authors concluded that the probable reason for this discrepancy between methods was water or oxide contamination of their calcium chloride.

3. Barium-barium chloride system

The barium-barium chloride system contains a liquid immiscibility gap with the consolute point at 1017°C. The eutectic horizontal occurred at 710°C and about 2 mole percent barium. The monotectic horizontal occurred at 890°C and 15 mole percent barium. The phase diagram is shown in Figure 7. Except for the solubility of barium chloride in barium metal at 900°C, this diagram was determined by thermal analysis. A sample containing 3 mole percent barium metal gave a thermal break at 946°C corresponding to the liquidus. A well defined break occurred between 919°C and 923°C which was interpreted as the barium chloride transformation. Several poorly defined breaks occurred between 926°C and 940°C which were probably due to one and two phase solid solution regions. The monotectic horizontal occurred at 890°C. The eutectic horizontal occurred at about 700°C and was very poorly defined. A sample containing 7 mole percent barium metal gave a break at 919°C with a larger break at 917°C. These breaks were interpreted as the liquidus and the α - β barium chloride transformation respectively. The eutectic break was very poorly defined and occurred around 700°C. A sample containing 15 mole percent barium metal gave a thermal halt at 890 corresponding to the monotectic composition and temperature. Samples containing 19.6, 34.0, 37.1, 50.3, 70.0 and 90.0 mole percent barium metal gave well

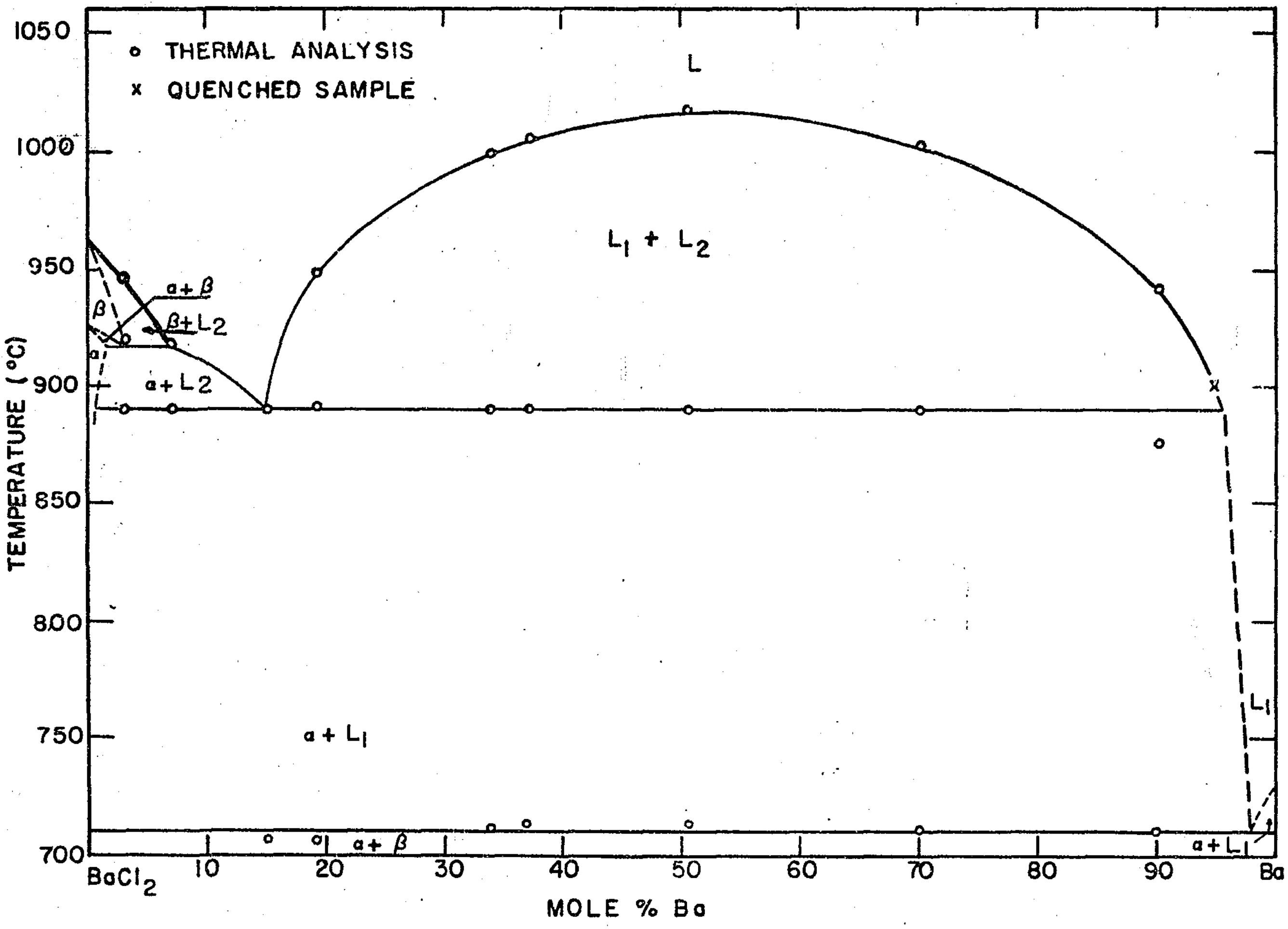

Figure 7. Barium-barium chloride phase diagram

Table 7. Thermal analysis of barium-barium chloride

Composition mole % Ba	Immiscibility gap boundary	Monotectic horizontal	Eutectic horizontal	Liquidus	Transformation
3.0		890	ca 700	946	919-923
7.0		890	ca 700	919	917
15.0	890	890	707	890	
19.6	948	891	706		
34.0	999	890	711		
37.1	1005	890	713		
50.3	1017	890	713		
70.0	1003	890	710		
90.0	942	875	710		

defined breaks corresponding to the boundary of the liquid immiscibility gap, monotectic horizontal and eutectic horizontal. The 90 mole percent monotectic horizontal was poorly defined due to the small amount of barium chloride in this sample. The results are summarized in Table 7.

The analysis of a sample of barium chloride and crude barium quenched from 900°C gave 20 mole percent barium dissolved in barium chloride and 5.2 mole percent barium chloride dissolved in the barium metal. This high solubility of barium metal in barium chloride was probably due to impurities such as barium oxide and nitride in the barium metal. Since work on the ternary isothermal sections indicated that the impurities in the crude barium had a negligible effect on the solubility of the salt in the metal, the value of 5.2 mole percent as the solubility of barium chloride in barium was accepted as being valid. A sample quenched from 950°C showed poor phase separation and it was not possible to determine the solubilities at this temperature by chemical analysis. At both 900°C and 950°C the density of the metal phase was greater than that of the salt phase. The diagram is in good agreement with the diagram reported by Schäfer (34). The monotectic temperature and the consolute point reported by Schäfer were 880°C and 1010°C respectively compared to 890°C and 1017°C found by this investigation. This diagram is in marked disagreement with the diagram reported by Eastman, et al. (17). These authors reported the monotectic to be at 840°C and 40 mole percent barium. The solubility of barium in barium chloride at 1000°C was given as 30 mole percent. The density of the metal phase was reported to be less than that of the salt phase.

4. Barium chloride-calcium chloride system

The barium chloride-calcium chloride system consists of an incongruently melting compound $BaCl_2 \cdot CaCl_2$ and an eutectic at 595°C and about 37 mole percent barium chloride. The phase diagram is shown in Figure 8. It was taken from Bukhalova and Bergman (16) and

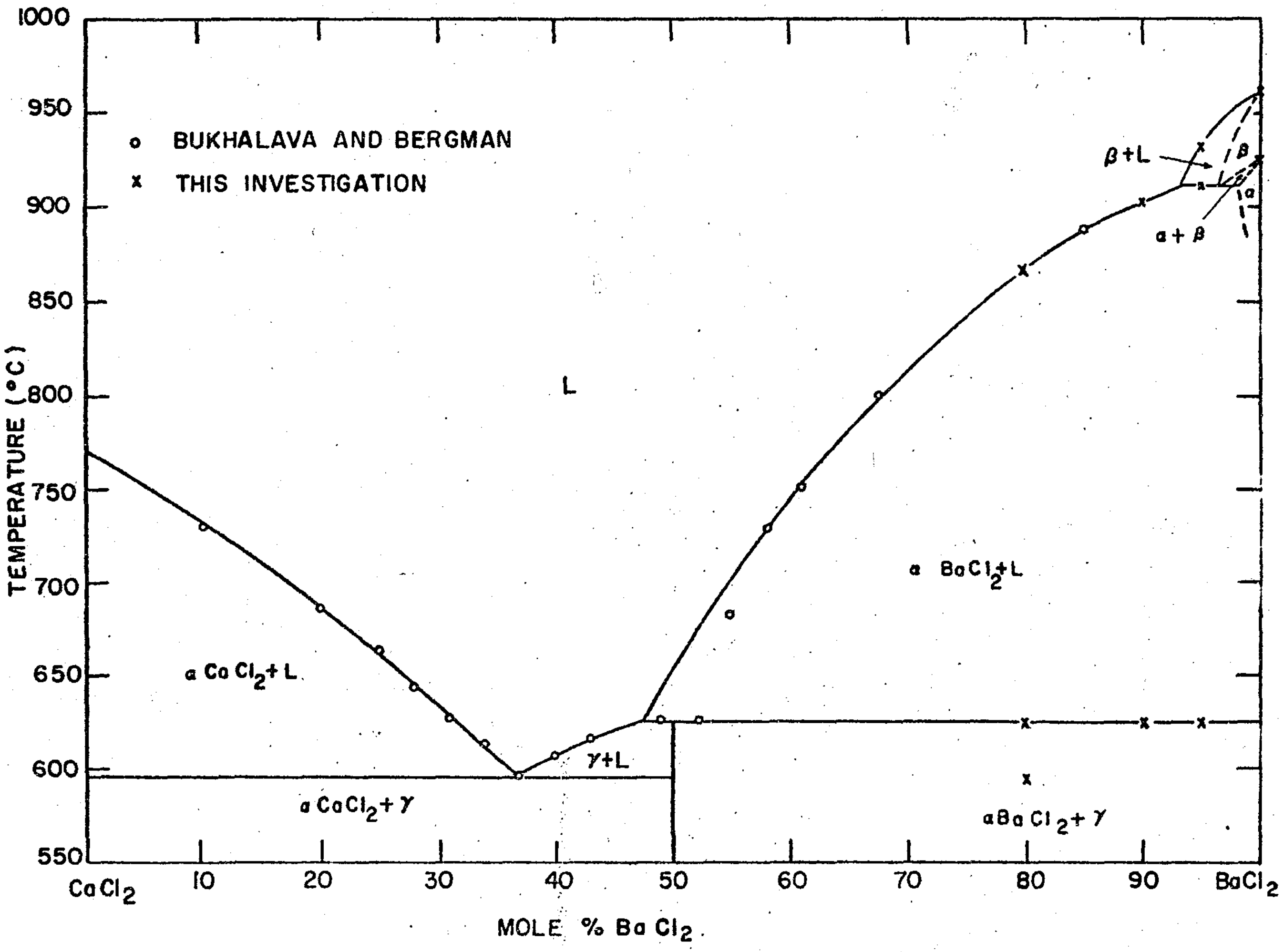

Figure 8. Calcium chloride-barium chloride phase diagram

was modified in that the reported congruently melting compound was changed to an incongruently melting compound and the α - β transformation of barium chloride was added. A sample of barium chloride containing 5 mole percent calcium chloride gave a thermal break at 933°C, an isothermal halt at 912°C, and another break at 625°C. These breaks were interpreted as the liquidus, α - β transformation and the peritectic horizontal. A sample of barium chloride containing 10 mole percent calcium chloride gave thermal breaks at 903°C and 625°C corresponding to the liquidus and the peritectic horizontal. A sample of barium chloride containing 20 mole percent calcium chloride gave breaks at 868°C, 625°C, and 595°C. When this sample was cooled from 900°C to 615°C and held at the latter temperature for 10 hours, the 595° break was not observed on subsequent cooling and heating but did occur again after heating above 625°C. These data were interpreted as evidence for the peritectic reaction:

$$BaCl_2 \text{ solid} + \text{melt} \rightleftharpoons BaCl_2 \cdot CaCl_2 \ .$$

On fast cooling, the compound formed around the barium chloride crystals and prevented the reaction from going to completion. The excess melt, being richer in calcium chloride, then gave the eutectic break on further cooling. When the sample was annealed at 615°C, the melt diffused through the compound and reacted completely with the solid barium chloride. The data reported by other investigators

Table 8. Compound and eutectic in the calcium chloride-barium chloride system

Investigator	Compound	Eutectic
This investigation	Peritectic 625°C	595°C
Ruff and Plato (21)	None	590°C and 37% $BaCl_2$
Sato and Amano (18)	None	617°C and 46% $BaCl_2$
Sandonnini (14)	None	595°C and 38% $BaCl_2$
Alabyshev and Lantratov (35)	None	Not reported
Budinkov, et al. (36)	Peritectic 632°C	605°C and 35% $BaCl_2$
Bukhalova and Bergman (16)	Congruent 629°C	594°C and 36.5% $BaCl_2$ 624°C and 54% $BaCl_2$

is summarized in Table 8.

B. Ternary System

1. The isothermal section at 900°C

The isothermal section was determined by analyzing the metal and salt phases from samples quenched from 900°C. One series of determinations was made at this temperature using calcium metal and barium chloride as the starting materials while another series was made with the crude barium and calcium chloride as the starting materials. Good agreement was obtained between the two series on the solubility of the salt in the metal phase. The solubility of the metal in the salt phase for the series prepared from barium metal and calcium chloride was about twice as great as the solubility obtained for the calcium-barium chloride series. In attempting to find the reason for this discrepancy, it was found by thermal analysis that the barium-barium chloride monotectic temperature rose above 900°C as the composition moved into the ternary system. As a result, two three phase regions consisting of solid barium chloride, liquid metal, and liquid salt must exist in this isothermal section. The composition of each of these phases must remain constant in this region since from the phase rule at constant temperature, three phases present in a three component system have zero degrees of freedom. A two phase region consisting of liquid metal and solid chloride lies between these two three phase regions. Thermal analysis also showed that the solubility found by the calcium-barium chloride series was of the correct magnetude. Since the crude barium calcium chloride samples undoubtedly had a larger impurity content and the solubility of the metal in the salt phase was twice that found by thermal analysis, the results of this series were considered incorrect. The increased solubility was probably due to oxygen, nitrogen, and carbon impurities in the crude barium because it was not observed when distilled barium used for thermal analysis and determination of the 950°C isothermal section. The metal phase boundary is probably correct since a good check was obtained over the region covered by both series of experiments. The calcium-barium chloride series covered a limited range of compositions because it is fixed on one side by a three phase region and on the other side by the high metal to salt ratio needed to obtain some compositions. The analytical data and the concentration quotients defined by:

$$C = \frac{N_{Ca_m}}{N_{Ba_m}} \times \frac{N_{Ba_s}}{N_{Ca_s}} \qquad \text{(equation 14)}$$

where N_{Ca_m} and N_{Ba_m} are the mole fractions of calcium and barium in the metal phase and N_{Ca_s} and N_{Ba_s} are the mole fractions of calcium and barium in the salt phase, are listed in Table 9. The isothermal section as determined by this data is shown in Figure 9. The dashed lines refer to the barium-calcium chloride data, the dotted lines are the estimated boundaries of the three phase regions, and the solid lines represent the calcium-barium chloride data.

2. The isothermal section at 950°C

The isothermal section was determined by analyzing the metal and salt phases of samples quenched from 950°C. Only two determinations were made with calcium metal and barium chloride as the starting materials because of the extremely high or low ratios of starting material needed to cover a very wide concentration range.

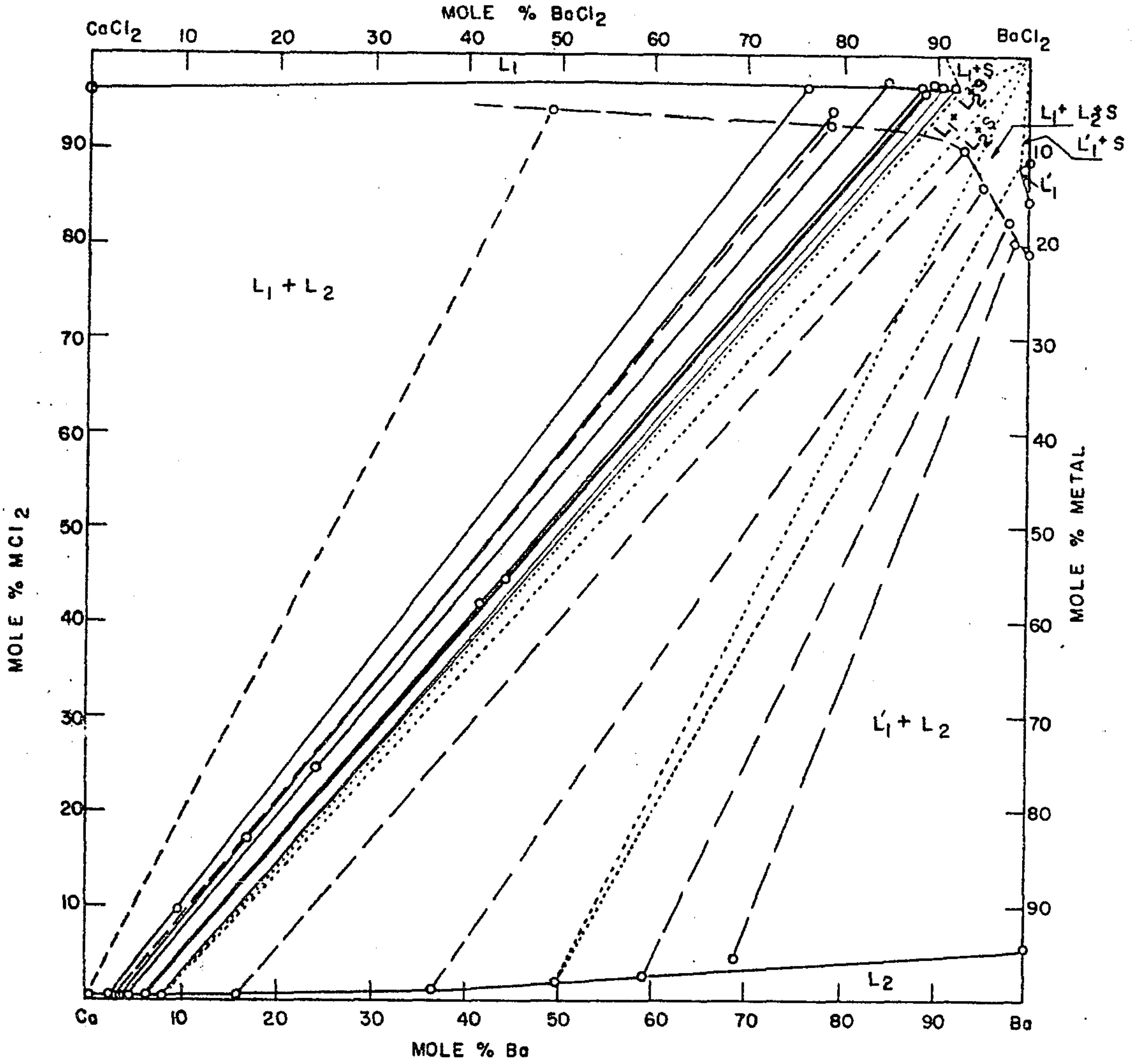

Figure 9. Isothermal section at 900°C

Table 9. Analytical data and concentration quotients at 900°C

Starting materials (grams)				Salt phase				Metal phase			C
Ca	Ba	$CaCl_2$	$BaCl_2$	% Cl	$\frac{\text{mole metal}}{\text{gram}}$ x 10^4	N_{Ba_s}	N_{metal}	% Cl	N_{Ba_m}	N_{MCl_2}	
	20.727	5.403		29.49	10.17	0.985	.196	2.86	0.690	0.044	27.1
	19.639	6.433		30.16	8.99	0.977	.174	1.82	0.594	0.025	30.7
	5.973	2.995		31.47	7.24	0.951	.139	0.90	0.367	0.01	35.3
	5.144	3.536		32.85	5.13	0.928	.010	0.79	0.159	0.0064	66.4
	9.306	8.579		35.96	4.03	0.787	.0736	0.69	0.0318	0.0043	108.0
	6.479	10.418		43.83	3.93	0.490	.060	1.09	0.0022	0.0064	483.0
2.430			19.213	34.59	1.64	0.920	.0326	0.84	0.081	0.0056	129.0
2.954			18.050	34.85	1.67	0.905	.0329	0.53	0.081	0.0036	107.0
4.063			16.840	35.05	1.60	0.896	.0314	0.58	0.063	0.0038	133.0
4.238			17.483	35.04	2.02	0.887	.0393	0.64	0.063	0.0042	117.0
5.188			19.270	35.45	1.78	0.884	.0369	0.575	0.063	0.0038	113.0
10.899			18.294	35.99	1.44	0.849	.0276	0.688	0.044	0.0044	122.0
11.698			12.597	36.22	3.36	0.789	.0615	0.773	0.038	0.0048	94.7
11.192			6.327	37.40	1.96	0.763	.0358	0.825	0.027	0.005	116.0

The other samples were prepared from double distilled barium metal and calcium chloride. Excellent agreement was obtained between the two sets of data. The concentration quotient was approximately constant with an average value of 82.3 up to about 90 mole percent barium in the salt phase. Between 90 and 99 mole percent barium in the salt phase, the solubility of the metal phase in the salt phase increased rapidly and the concentration quotient decreased from about 82.3 at 90 mole percent to 15.1 at 99 mole percent barium in the salt phase. This decrease in the concentration quotient was attributed to the high solubility of the metal phase in the salt phase. The analytical data and the concentration quotients are presented in Table 10. A comparison of the two methods for analyzing the metal phase is shown in Table 11. The fractional estimated standard deviation, defined as:

$$S = \frac{\sqrt{\frac{\sum_{i=1}^{n} (C_i - \bar{C})^2}{n - 1}} \times 100}{\bar{C}} \qquad \text{(equation 15)}$$

where n is the number of samples, C_i is the ith value of the concentration quotient and $\bar{C}$ is the average value of the concentration quotient, was calculated for both methods for sample with less than 90 mole percent barium in the salt phase. For the sulfate method, the fractional estimated standard deviation was 14.6 percent while for the material balance method, the fractional estimated standard deviation was 5.0. This shows that the material balance method is more

Table 10. Analytical data and concentration quotients at 950°C

Starting materials (grams)				Salt phase				Metal phase			C
Ca	Ba	$CaCl_2$	$BaCl_2$	% Cl	mole metal / gram x 10^4	N_{Ba_s}	N_{Metal}	% Cl_2	N_{Ba_m}	N_{MCl_2}	
	16.233	2.006		27.28	14.82	0.990	0.278	4.53	0.856	0.082	15.1
	14.946	4.888		30.88	7.36	0.983	0.145	1.87	0.588	0.027	40.5
	14.078	7.421		32.17	5.31	0.964	0.105	1.51	0.335	0.016	53.2
2.731			17.920	34.80	2.12	0.895	0.041	1.0	0.096	0.0071	80.3
	7.002	5.956		35.52	2.20	0.885	0.042	1.0	0.070	0.0067	78.4
4.934			9.925	35.85	2.06	0.841	0.039	1.05	0.056	0.0068	89.1
	4.842	6.037		40.45	2.68	0.613	0.045	2.06	0.019	0.012	81.6
	6.909	11.946		44.94	1.97	0.454	0.030	1.61	0.010	0.009	82.3
	3.016	11.806		53.28	3.12	0.201	0.040	2.21	ca 0.003	ca 0.012	ca 84.0

Table 11. Comparison of metal phase analyses

Salt phase		Metal phase Sulfate method			Metal phase Material balance method		
N_{Ba_s}	$N_{(OH)_2^=}$	N_{Ba}	N_{MCl_2}	C	N_{Ba_m}	N_{MCl_2}	C
0.990	0.278	0.886	0.085	13.6	0.856	0.082	15.1
0.983	0.145	0.616	0.027	36.8	0.588	0.027	40.5
0.964	0.105	0.354	0.016	48.2	0.335	0.016	53.2
0.895	0.041	0.108	0.0072	71.9	0.096	0.0071	80.3
0.885	0.042	0.0855	0.0069	63.1	0.070	0.0067	78.4
0.841	0.039	0.0657	0.0070	71.2	0.056	0.0068	89.1
0.613	0.045				0.019	0.012	81.6
0.454	0.030	0.00942	0.0095	86.8	0.010	0.009	82.3
			$\bar{C}$ = 73.3			$\bar{C}$ = 82.3	
			S = 14.6			S = 5.0	

precise.

The isothermal section as determined by these data is shown in Figure 10. The solubility of the salt phase in the metal phase gave a smooth curve with a slight minimum at about 10 atomic percent barium. The solubility of the metal phase in the salt phase also showed a minimum which occurred at about 50 mole percent barium in the salt. The point at 61.3 mole percent barium was determined with barium metal which had been exposed to the atmosphere of the dry box several times and possibly had become contaminated by water vapor causing the higher solubility. The observed solubility of metal phase in the salt at 99 mole percent barium in the salt phase was about 11 mole percent higher than that predicted by the solubility curve. This error probably due to two causes. In all of the ternary samples, the metal phase was less dense than the salt phase but in the barium-barium chloride binary system the metal phase was more dense than the salt phase. Therefore somewhere in the region around 99 mole percent barium in the salt phase, the density of the two phases must be equal and it would be impossible to separate the two phases. The other cause of this high solubility was the high metal to salt ratio needed to reach this composition. The small amount of oxygen, nitrogen and water in the barium metal would be appreciable compared to the small amount of salt. The two phase solid barium chloride +

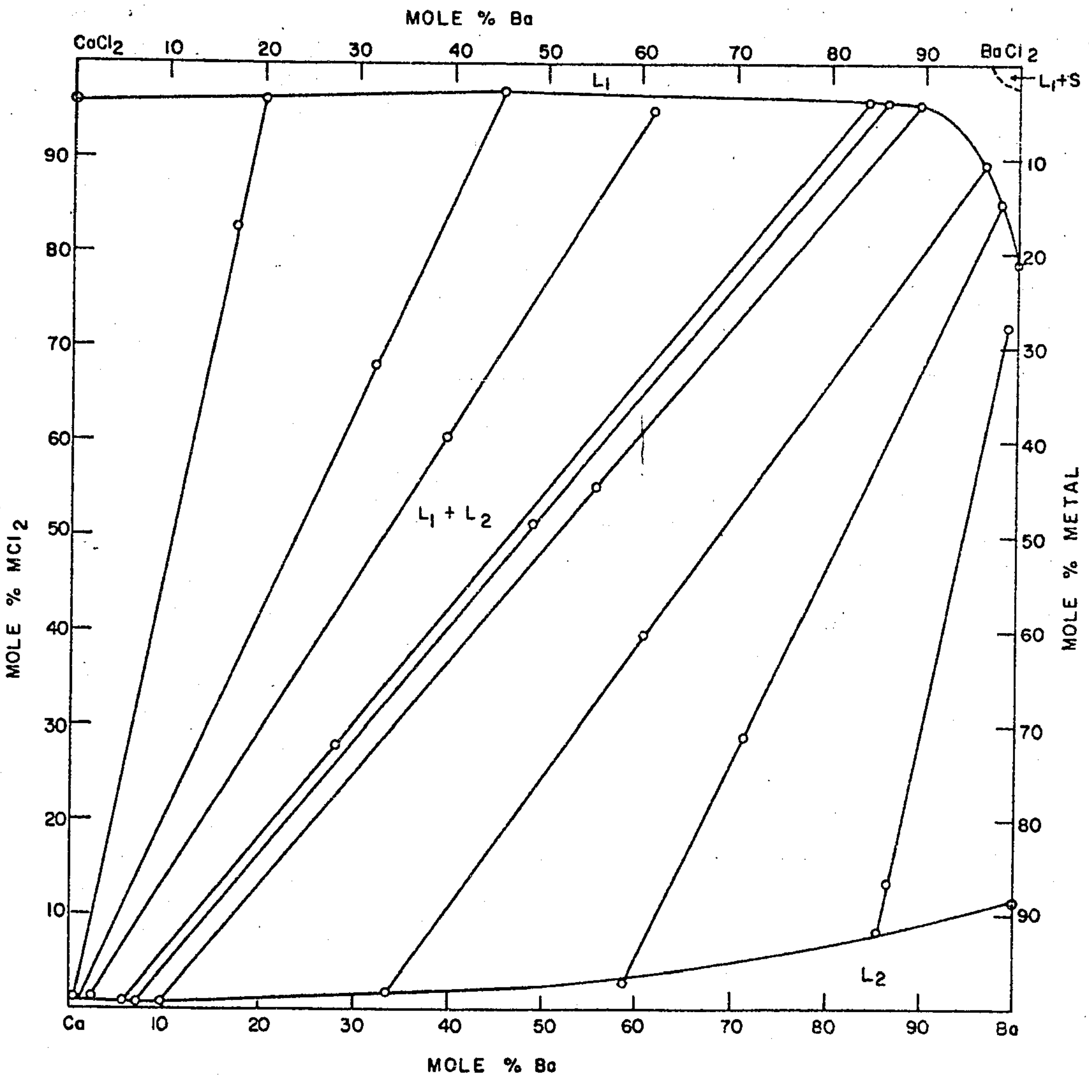

Figure 10. Isothermal section at 950°C

liquid salt region was estimated from the barium chloride-barium and barium chloride-calcium chloride binary systems.

3. Prediction of ternary solubility of metal in the salt phase

In this type of ternary metathetical system at temperatures where a liquid salt and liquid metal phase exist, the phases in equilibrium can be shown as tie-lines in an isothermal section. For systems in which the solubility of the metal phase in the salt phase and the solubility of the salt phase in the metal phase is negligible, the data may be presented as an equation giving the concentration quotient as a function of the concentration of one of the species. If one of the solubilities is not negligible, a means must be provided to calculate this solubility in order to analytically describe the isothermal section. For this system, the solubility of metal in the salt phase was not negligible. In order to find an equation which would predict this solubility, several hypotheses as to how the metal dissolved or existed in the salt phase were considered. Solubility curves were calculated and compared with the experimental curve to see which model would best explain the observed variation of solubility with composition.

The hypotheses used to calculate the solubility of the metal phase in the salt phase imply that the salt phase can be considered to be composed of individual species of calcium, barium, barium chloride and calcium chloride. The observed concentration quotients can be corrected for the amount of dissolved calcium and barium metal by subtracting the calculated amount of each metal from the total amount of that element in the salt phase. The calculated equilibrium constants were then compared to see which set was most nearly independent of concentration.

The following assumptions were common to all of the models. (1) Calcium metal and barium metal form an ideal solution with each other. This assumption was probably valid as the two metals are quite similar and form a continuous series of solid solutions. (2) Calcium chloride and barium chloride form an ideal binary solution. This assumption is probably good because the intermolecular forces should be weak since only an incongruent intermolecular compound is formed which decomposes about 350°C below the operating temperature. Also, Rinck's work (10) indicates that sodium and potassium halides probably form ideal solutions. (3) The salt that dissolves in the metal obeys Henry's law. This assumption implies that the activity of the metal in metal phase is equal to the mole fraction. The results would not be appreciably changed if this were not true since the salt solubility was less than two percent for most of these compositions.

The first model was based on the assumption that monochloride monomers were formed as follows:

$$Ca + CaCl_2 \rightleftharpoons 2\ CaCl \qquad \text{(equation 15)}$$

$$Ba + BaCl_2 \rightleftharpoons 2\ BaCl \qquad \text{(equation 16)}$$

It was also assumed that these monochlorides form ideal solutions with the salt phase and obey Henry's law in the metal phase in both the binary and ternary systems. The equilibrium constants for the formation of the monochlorides can be calculated from the binary solubilities with the following equations:

$$k_{CaCl} = \frac{N^2_{CaCl}}{N_{Ca} N_{CaCl_2}} \qquad \text{(equation 17)}$$

and

$$k_{BaCl} = \frac{N^2_{BaCl}}{N_{Ba} N_{BaCl_2}} \qquad \text{(equation 18)}$$

Since

$$N_{Ba_s} = N_{BaCl_2} + N_{BaCl} \qquad \text{(equation 19)}$$

and

$$N_{Ca_s} = N_{CaCl_2} + N_{CaCl} \qquad \text{(equation 20)}$$

These equations may be combined with equations 17 and 18 to give the concentrations of calcium chloride and barium chloride as follows:

$$N_{CaCl_2} = N_{Ca_s} + \frac{k_{CaCl} N_{Ca}}{2} - \sqrt{N_{Ca_s} N_{Ca} k_{CaCl} + \left(\frac{k_{CaCl} N_{Ca}}{2}\right)^2} \qquad \text{(equation 21)}$$

$$N_{BaCl_2} = N_{Ba_s} + \frac{k_{BaCl}N_{Ba}}{2} - \sqrt{N_{Ba_s}N_{Ba}k_{BaCl} + \left(\frac{k_{BaCl}N_{Ba}}{2}\right)^2}$$

(equation 22)

These values of N_{CaCl_2} and N_{BaCl_2} may be used in equation 6 to calculate the reaction equilibrium constants. Substituting values of the solubility from the binary systems into equations 17 and 18 gave the following values of the equilibrium constants for the monochlorides.

$$k_{CaCl} = 7.95 \times 10^{-3}$$

$$k_{BaCl} = 0.395$$

By using a value of the equlibrium constant calculated from the tie-line at 89.5 mole percent barium in the salt, the composition of the salt phase for various metal phase compositions was calculated and the curve obtained was compared with the experimental curve. Due to the complexity of equations 21 and 22, the composition of the salt phase was determined by successive approximations. The calculated curve is shown in Figure 11. Since this model predicted solubilities in the salt as much as four times greated than the observed solubilities, the equilibrium constants were not calculated.

The second model was based on the assumption that monochloride dimers were formed as follows:

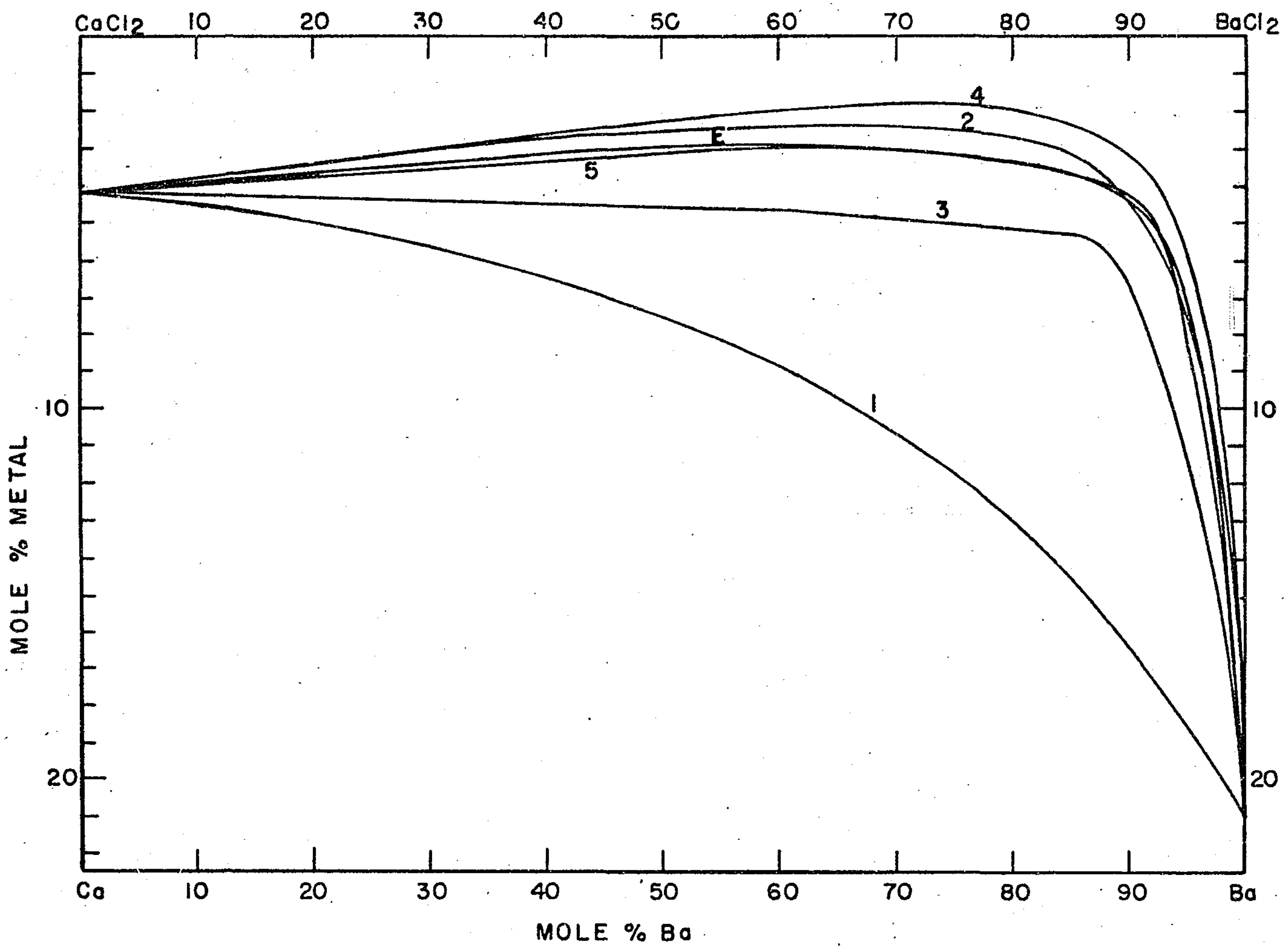

Figure 11. Calculated solubility curves

$$Ca + CaCl_2 \rightleftharpoons (CaCl)_2 \qquad \text{(equation 23)}$$

and

$$Ba + BaCl_2 \rightleftharpoons (BaCl)_2 \qquad \text{(equation 24)}$$

The equilibrium constants for formation of the monochlorides were calculated from the binary solubilities with the following equations.

$$k_{(CaCl)_2} = \frac{N_{(CaCl)_2}}{N_{Ca} N_{CaCl_2}} \qquad \text{(equation 25)}$$

and

$$k_{(BaCl)_2} = \frac{N_{(BaCl)_2}}{N_{Ba} N_{BaCl_2}} \qquad \text{(equation 26).}$$

Since

$$N_{Ba_s} = N_{BaCl_2} + 2\, N_{(BaCl)_2} \qquad \text{(equation 27)}$$

and

$$N_{Ca_s} = N_{BaCl_2} + 2\, N_{(CaCl)_2} \qquad \text{(equation 28)}$$

these equations may be combined with equations 25 and 26 to give:

$$N_{CaCl_2} = \frac{N_{Ca_s}}{1 + 2\, k_{(CaCl)_2} N_{Ca}} \qquad \text{(equation 29)}$$

and

$$N_{BaCl_2} = \frac{N_{Ba_s}}{1 + 2\, k_{(BaCl)_2} N_{Ba}} \qquad \text{(equation 30).}$$

Substituting the equations for N_{CaCl_2} and N_{BaCl_2} into equation 6, the following equation for the reaction equilibrium constant was obtained:

$$K = \frac{N_{Ca}}{N_{Ba}} \times \frac{N_{Ba_s}}{N_{Ca_s}} \left(\frac{1 + 2\, k_{(CaCl)_2} N_{Ca}}{1 + 2\, k_{(BaCl)_2} N_{Ba}} \right) \qquad \text{(equation 31).}$$

Table 12. Corrected reaction equilibrium constants

Concentration quotients	Model 2	Model 3	Model 4	Model 5
87.9	96.1	92.9	91.4	92.5
77.6	83.4	85.9	80.6	82.6
82.9	85.4	99.2	85.0	93.2
67.8	68.4	82.7	69.0	76.5
76.7	76.0	98.8	77.4	89.6
53.2	44.3	220	49.7	71.4
40.5	27.6	597	35.6	65.1

The equilibrium constants for formation of calcium and barium monochlorides were 0.0473 and 0.470 respectively.

Using the value of K obtained from the tie-line at 89.5 mole percent barium in the salt phase and arbitrary values of N_{Ba}, the compositions of the salt phase were calculated and the resulting curve is shown in Figure 11. The corrected equilibrium constants are shown in Table 12.

Model 3 was based on the assumption that the calcium and barium dissolved in the salt phase according to Henry's law, i.e.

$$N_{Ca^{\circ}_{s}} = k_1 N_{Ca} \qquad \text{(equation 32)}$$

and

$$N_{Ba^{\circ}_{s}} = k_2 N_{Ba} \qquad \text{(equation 33)}$$

where $N_{Ca^\circ_s}$ and $N_{Ba^\circ_s}$ are the mole fractions of metallic calcium and barium dissolved in the salt. The Henry's law constants were calculated from the respective binary solubilities as follows:

$$k_1 = \frac{N_{Ca^\circ_s}}{N_{Ca}} = 0.0427$$

and

$$k_2 = \frac{N_{Ba^\circ_s}}{N_{Ba}} = 0.237.$$

Since

$$N_{Ba_s} = N_{BaCl_2} + N_{Ba^\circ_s} \qquad \text{(equation 34)}$$

and

$$N_{Ca_s} = N_{CaCl_2} + N_{Ca^\circ_s} \qquad \text{(equation 35),}$$

These equations were combined with equations 32 and 33 to give:

$$N_{CaCl_2} = N_{Ca_s} - k_1 N_{Ca} \qquad \text{(equation 36)}$$

and

$$N_{BaCl_2} = N_{Ba_s} - k_2 N_{Ba} \qquad \text{(equation 37).}$$

Combining equations 36 and 37 with equation 6 gives:

$$K = \frac{N_{Ca}}{N_{Ba}} \; \frac{(N_{Ba_s} - k_2 N_{Ba})}{(N_{Ca_s} - k_1 N_{Ca})} \qquad \text{(equation 38).}$$

From this equation, corrected equilibrium constants could be calculated. Using the value of K obtained from the tie-line at 89.5 mole percent barium in the salt phase, the solubility curve was calculated and is shown in Figure 11. Since this model predicted higher solubilities than were observed, the concentrations quotients were corrected by modifying this model to use the observed solubilities. It was assumed that the ratio of calcium metal to barium metal dissolved in the salt phase was equal to the ratio of these metals in the metal phase multiplied by the ratio of the Henry's law constants, i.e.,:

$$\frac{N_{Ca^\circ_s}}{N_{Ba^\circ_s}} = \frac{k_1}{k_2} \left(\frac{N_{Ca}}{N_{Ba}}\right) \qquad \text{(equation 39).}$$

Since

$$N_{M^\circ_s} = N_{Ca^\circ_s} + N_{Ba^\circ_s} \qquad \text{(equation 40)}$$

where $N_{M^\circ_s}$ is the total metal dissolved in the salt phase, the values of $N_{Ca^\circ_s}$ and $N_{Ba^\circ_s}$ were calculated and substituted into equations 34 and 35 to give N_{CaCl_2} and N_{BaCl_2}. These values were used with equation 6 to calculate the corrected equilibrium constants shown in Table 12.

The fourth model was a modified Henry's law. It was assumed that calcium metal only dissolved in calcium chloride and barium metal dissolved in barium chloride. The amounts of each metal dissolved were given by the following equations:

$$N_{Ca^\circ_s} = k'_1 N_{Ca} N_{CaCl_2} \qquad \text{(equation 41)}$$

and

$$N_{Ba^\circ_s} = k'_2 N_{Ba} N_{BaCl_2} \qquad \text{(equation 42).}$$

Equations 41 and 42 were combined with equations 34 and 35 to give:

$$N_{CaCl_2} = \frac{N_{Ca_s}}{1 + k_1' N_{Ca}} \qquad \text{(equation 43)}$$

and

$$N_{BaCl_2} = \frac{N_{Ba_s}}{1 + k_2' N_{Ba}} \qquad \text{(equation 44).}$$

These equations were substituted into equation 6 to give:

$$K = \frac{N_{Ca}}{N_{Ba}} \; \frac{N_{Ba_s}}{N_{Ca_s}} \; \frac{1 + k_1' N_{Ca}}{1 + k_2' N_{Ba}} \qquad \text{(equation 45)}$$

The Henry's law constants were as follows:

$$k_1' = 0.0445$$

$$k_2' = 0.30$$

The values of the corrected reaction equilibrium constants are listed in Table 12. By using the value of K obtained from the tie-line at 89.5 mole percent barium, the solubility curve was calculated and is shown in Figure 11.

Since model 3 gave equilibrium constants which increased at high barium compositions while model 4 gave corrected equilibrium constants which decreased even more than the observed concentration quotients an intermediate Henry's law model was tried. It was assumed in this model that barium dissolved according to model 3 and calcium dissolved according to the following equation:

$$N_{Ca^\circ_s} = k_1 N_{Ca} (N_{CaCl_2} + a N_{BaCl_2}) \quad \text{(equation 46)}$$

where a was an empirical constant which was adjusted to give the correct solubility at one point on the solubility curve. A value of a = 0.4 gave the correct solubility at 89.5 mole percent barium in the salt phase. The corrected equilibrium constants are listed in Table 12 and the solubility curve is shown in Figure 11.

A comparison of the curves in Figure 11 shows that the monochloride monomer, model 1, predicted much higher solubilities than were observed and this model was discarded. The monochloride dimer, model 2, gave a good qualitative fit to the experimental solubility curve. The major weakness of this model was that the resulting equilibrium constants decreased even more than the observed concentration quotients. Since the monochloride monomers gave too high a solubility while the dimers gave a low solubility, another model is possible which assumes an equilibrium between the dimer and monomer species. However, it is not possible to evaluate the two equilibrium constants for the formation of both monomer and dimer monochlorides from one binary system and this model was not used.

The simple Henry's law, model 3, gave a fair estimate of the solubility but it was qualitatively incorrect in that the predicted solubility did not decrease below the value for the calcium-calcium chloride binary. The second Henry's law, model 4, gave the correct shape for the curve but predicted a lower solubility than was observed. The corrected equilibrium constants also decreased more than the experimental concentration quotients. The combined Henry's law, model 5, gave the best fit to the solubility curve and the most nearly constant equilibrium constants. However, since it contained an adjustable constant, a better agreement with the experimental data would be expected.

These calculations show that the isothermal sections can be described approximately in this system by assuming that the salt and metal phases obey the ideal law of mass action and that the two metals dissolve independently in the salt. The solubility behavior indicates that calcium interacts more strongly with calcium chloride than with barium chloride. No difference between the interaction of barium chloride and calcium chloride with barium could be detected due to the extent of the equilibrium reaction. The state of the dissolved metal in the salt phase can not be deduced from the solubility data.

4. Standard free energy and enthalpy change for the reaction of barium with calcium chloride

From a knowledge of the equilibrium constant at two temperatures, the standard free energy change at both temperatures and the enthalpy change of the reaction may be calculated with equations 3 and 5 respectively. If it is assumed that the equilibrium constant is equal to the concentration quotient in the region of low solubility, the free energy may be calculated. This assumption is probably good since in this region, all of the solubility models except the monochloride monomers gave about the same value for the equilibrium constant as the concentration quotient. The calcium-barium chloride data at 900°C gave an average equilibrium of 116.5 ± 10 with the corresponding free energy change equal to -11.1 k cal. Using only the data up to 90 mole percent barium in the salt phase, the average value of the equilibrium constant at 950°C is equal to 82.3 ± 4.1 and the corresponding value of the free energy change is -10.7 k cal. From these values of the equilibrium constant, the enthalpy change of the reaction was calculated to be -19.9 k cal per gram atom of metal. The standard state of all components is the pure liquid.

These values of the equilibrium constant free energy change, and enthalpy change are compared with values computed from compiled thermodynamic data in the literature in Table 13. The variation in the computed values of the standard free energy of the reactions is due to different estimates of the standard entropy of barium chloride at 25°C and of the heats of transition of the pure metals and salts.

Table 13. ΔF, ΔH, and K for the reaction of barium with calcium chloride

Investigator	K		ΔF(k cal)		ΔH(k cal)
	900°C	950°C	900°C	950°C	
This investigation	116.5	82.3	-11.1	-10.7	-19.9
Brewer, et al. (37)	38.2	30.2	- 8.5	- 8.3	-16.6
Glassner (38)	73.0	50.9	-10.0	- 9.6	-19.0
Villa (39)	273	201	-13.0	-12.9	-15.4

5. Polythermal ternary projection

One method of showing a three dimensional temperature-composition ternary system in two dimensions is a polythermal projection. In this projection, the intersections of the various surfaces are drawn in the composition plane with arrows indicating the direction of composition change with decreasing temperature. The polythermal projection of the calcium-barium-barium chloride-calcium chloride system is shown in Figure 12. In the barium chloride corner of the projection, a curve extends from 6.6 mole percent calcium chloride on the calcium chloride-barium chloride system to 7.0 mole percent barium on the barium-barium chloride system representing the intersection of the α barium chloride liquidus surface with the β barium chloride liquidus surface. This curve contains a maximum at

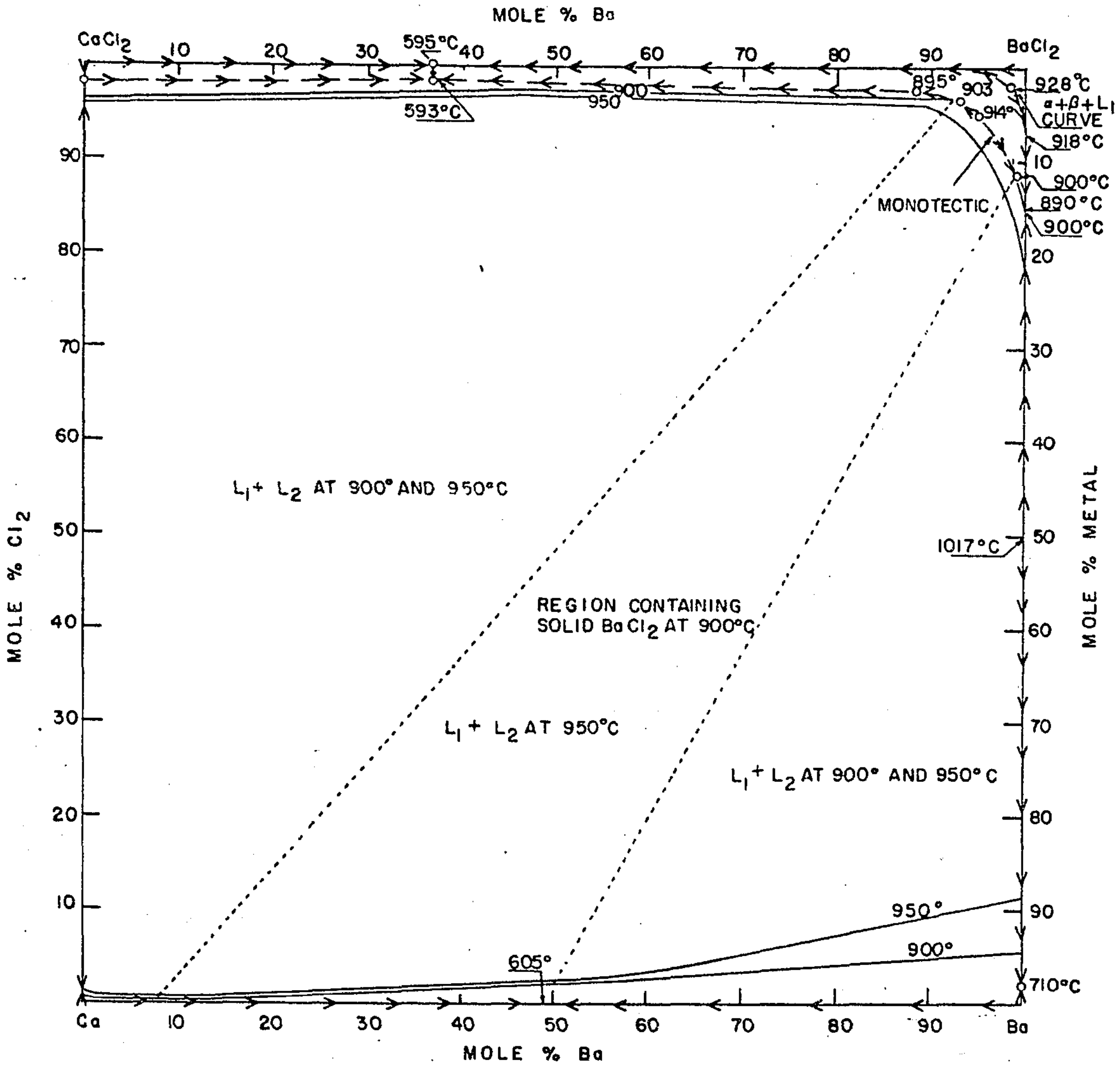

Figure 12. Polythermal projection of the barium-calcium chloride system

about 928°C and 1.5 mole percent calcium and 1.5 mole percent metal. The curve then drops to 918°C on the barium-barium chloride binary and 912°C on the calcium chloride-barium chloride binary. Since the α - β transformation was lowered on both binaries, the solubility of barium metal and of calcium chloride must lower in the low temperature α barium chloride than in the high temperature β barium chloride. Since the transformation is raised in the ternary system, the relative solubility seems to be reversed so that the solubility in α is greater than in β.

The monotectic curve is produced by the intersection of the salt liquidus surface with the two liquid surface. This curve starts at 890°C and 15 mole percent barium on the barium-barium chloride binary and rises to 915°C at about 5 mole percent metal and 5 mole percent calcium in the ternary system. The curve decreases to 895°C at 2.8 mole percent metal and 11.5 mole percent calcium. The curve is then estimated down to the ternary eutectic point at 593°C and about 1.6 mole percent metal and 63 mole percent calcium. The eutectic line is estimated up to the calcium-calcium chloride eutectic. The 900°C isothermal boundary of the liquid salt and 2 liquid regions shows how it intersects the monotectic to produce the solid salt region. The boundaries of this solid region also indicate the general direction of the tie-lines in the 900°C and 950°C isotherms. The 900° and 950° boundaries of the immiscibility gap are also shown.

IV. SUMMARY

The reaction of barium with calcium chloride was investigated by determining the calcium-barium-barium chloride-calcium chloride ternary system. Isothermal sections at 900° and 950° were determined by heating mixtures of calcium metal and barium chloride or barium metal and calcium chloride in capsules of 309 stainless steel, quenching in cold water and analyzing the metal and salt phases. The results were reported as isothermal tie-lines and as concentration quotients in which total calcium and barium concentrations in each phase were used. The concentration quotient was nearly independent of concentration between 0 and 90 mole percent barium in the salt phase with values of 116.5 and 82.3 at 900°C and at 950°C respectively in this region. Between 90 and 100 mole percent barium in the salt phase, the solubility of the metal in the salt increased rapidly and the concentration quotient at 950°C decreased to 40.5 at 98.5 mole percent barium chloride. At 950°C, the solubility of the salt in the metal phase decreased from 1.56 mole percent for pure calcium to 0.7 mole percent at 10 mole percent barium in the metal phase. The solubility then increased to 2.5 mole percent at 60 mole percent barium in the metal phase and 11.5 mole percent for pure barium. The solubility of metal in the salt was 4.2 mole percent for pure calcium chloride, decreased to 3 mole percent for 45 mole percent barium in the salt phase, increased to 4.2 mole percent for 90 mole percent barium and then increased to 21 mole percent for pure barium chloride. The experimental solubility of metal in the salt phase was compared with solubilities calculated by assuming that the two metals and the two salts form ideal solutions and making various assumptions as to how the metal dissolved in the liquid salt. Five models were considered; (1) monochloride monomers, (2) monochloride dimers, (3) the metal dissolved according to Henry's law, i.e., mole fraction of metal A dissolved in the salt is equal to a constant times the mole fraction of metal A in the metal phase, (4) the concentration of metal A dissolved in the salt phase was equal to a constant times the product of the mole fraction of metal A in the metal phase and the mole fraction of salt $A Cl_2$ in the salt phase, and (5) the barium metal dissolved according to model 3 and the mole fraction of calcium dissolved in the salt was equal to a constant times the product of the mole fraction of calcium in the metal phase and the sum of the mole fraction of calcium chloride plus an arbitrary constant times the mole fraction of barium chloride. This arbitrary constant was evaluated from one point on the ternary solubility curve. The equilibrium constant for the formation of the monochlorides and the Henry's law constants were calculated from the binary solubilities. Model 1 predicted solubilities as much as a factor of four greater than the observed solubility and was discarded. Models 2 and 4 gave good qualitative agreement with 2 being slightly better than 4. These models predicted lower solubilities than were observed. Model 3 gave fair agreement but overestimated the solubility by about 50 percent. The major weakness of this model was that the calculated solubility was never less than the solubility of calcium in calcium chloride. Model 5 gave good agreement with the observed solubility. These models were used to correct the apparent equilibrium constant for solubility of metal in the salt. Models 2 and 4 were of such a form that the correction further decreased the equilibrium constant in the region of 90 to 99 mole percent barium chloride. By modifying model 3 so that the observed solubility of metal could be used, the equilibrium constant was over-corrected in the region of 90 to 99 mole percent barium chloride. Model 5 gave a fairly constant equilibrium constant.

Thermal analysis was used to determine phase boundaries of the ternary system and to check the reported binary phase diagrams. In the barium-barium chloride system, the α - β transformation was lowered from 926° for pure barium chloride to 920°C, the consolute point was at 1017°C and 50 mole percent barium, the monotectic was at 890°C and 15 mole percent barium, and the eutectic was at 712°C and about 96 mole percent barium. In the calcium-calcium chloride system, the monotectic occurred at 820°C and more than 99 mole percent calcium. The eutectic occurred at 768°C and less than two mole percent calcium. The boundaries of the liquid immiscibility gap rose very steeply to values of 5 and 97.5 mole percent calcium at 1025°C. In the barium chloride-calcium chloride system the eutectic occurred at 595°C and 37 mole percent barium chloride, the α - β transformation was lowered to 910°C and the compound $CaCl_2 \cdot BaCl_2$ had an incongruent melting point at 625°C.

In the ternary system, the α - β transformation in barium chloride was raised from 920°C and 910°C in the binaries to 928°C at 1.5 mole percent calcium and 1.5 mole percent metal. The monotectic was raised from 890°C at 15 mole percent barium in the barium-barium chloride binary to 914°C at 5 mole percent calcium and 5 mole percent metal. It then drops to 895°C at 11.5 mole percent calcium and 2.5 mole percent metal. The ternary eutectic was at 593°C and about 1.65 mole percent metal and 37 mole percent calcium chloride.

Assuming that the concentration quotient was equal to the equilibrium constant in the region of low solubility, $\Delta F°$ for the reaction was equal to -11.1 and -10.7 k cal at 900°C and 950°C respectively. From these values of $\Delta F°$, $\Delta H°$ was calculated to be -19.9 k cal.

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VII. APPENDIXES

Appendix A. Derivation of equation 10

The amount of calcium in the salt phase was calculated from the chloride analysis and the amount of metal dissolved in the salt with equation 10. This equation was derived as follows:

$$\% \text{ Ca} + \% \text{ Ba} = 100 - \% \text{ Cl}$$

$$\text{moles Ca} + \text{moles Ba} = \text{moles salt} + \text{moles metal}$$

or

$$\frac{\% \text{ Ca}}{40.08} + \frac{\% \text{ Ba}}{137.36} = \frac{\% \text{ Cl}}{70.914} + M_M \,.$$

where M_M is the number of moles of metal dissolved in an 100 gram sample.

$$\% \text{ Ba} = 137.36 \left(\frac{\% \text{ Cl}}{70.914}\right) + M_M - \% \text{ Ca}/40.08$$

Substituting into the first equation gives

$$\% \text{ Ca} - \left(\frac{137.36}{40.08}\right) \% \text{ Ca} + 137.36 \left(\frac{\% \text{ Cl}}{70.914}\right) + M_M = 100 - \% \text{ Cl}$$

$$\% \text{ Ca} = \frac{100 - \% \text{ Cl} - 137.36 \left(\frac{\% \text{ Cl}}{70.914}\right) + M_M}{1 - 137.36/40.08}$$

$$\% \text{ Ca} = \frac{\frac{\% \text{ Cl}}{70.914} + M_M - \frac{100 - \% \text{ Cl}}{137.36}}{\frac{137.36 - 40.08}{40.08 \times 137.36}}$$

$$\%\ \mathrm{Ca} = \frac{\dfrac{\%\ \mathrm{Cl}}{70.914} + M_M - \dfrac{100 - \%\ \mathrm{Cl}}{137.36}}{.01767} \qquad \text{(equation 10)}$$

Appendix B. Derivation of equation 11

The amount of calcium in the metal phase was determined by means of equation 11 from the chloride analysis and the total calcium and barium content. The total calcium and barium content was measured by a gravimetric determination of the combined sulfate precipitate. This equation was derived as follows:

$$\% \mathrm{Ca} + \% \mathrm{Ba} = 100 - \% \mathrm{Cl}$$

$$\% \mathrm{Ca} \times \frac{\mathrm{CaSO_4}}{\mathrm{Ca}} + \% \mathrm{Ba} \times \frac{\mathrm{BaSO_4}}{\mathrm{Ba}} = \text{wt. of metal sulfates in a 100 gram sample.}$$

or $$3.3967 \% \mathrm{Ca} + 1.6993 \% \mathrm{Ba} = \text{wt. } \mathrm{M\,SO_4}$$

Since $$\% \mathrm{Ba} = 100 - \% \mathrm{Cl} - \% \mathrm{Ca},$$

$$3.3967 \% \mathrm{Ca} + (100 - \% \mathrm{Cl} - \% \mathrm{Ca}) \times 1.6993 = \text{wt. } \mathrm{M\,SO_4}$$

$$(3.3967 - 1.6993) \% \mathrm{Ca} = \text{wt. } \mathrm{M\,SO_4} - 1.6993\,(100 - \% \mathrm{Cl})$$

$$\% \mathrm{Ca} = \frac{\text{wt. } \mathrm{M\,SO_4} - 1.6993\,(100 - \% \mathrm{Cl})}{1.6974} \qquad \text{(equation 11)}$$

Appendix C. Derivation of equations 12 and 13

The amount of calcium and barium in the metal phase was also determined by using equations 12 and 13 with a material balance between the initial overall composition and the salt phase composition. These equations were derived as follows:

$$N_{MCl_2} = \frac{\%\ Cl/70.914}{\text{moles } MCl_2 + \text{moles metal}}$$

$$N_{Ca} = \frac{\%\ Ca/40.08}{\text{moles Ca} + \text{moles Ba}}$$

Since moles MCl_2 + moles metal = moles Ca + moles Ba,

$$\frac{\%\ Ca}{N_{Ca} \times 40.08} = \frac{\%\ Cl}{70.914 \times N_{MCl_2}}$$

$$\%\ Ca = \frac{N_{Ca} \times 40.08 \times \%\ Cl}{70.914 \times N_{MCl_2}} \qquad \text{(equation 12)}$$

also

$$N_{Ba} = \frac{\%\ Ba/137.36}{\text{moles Ca} + \text{moles Ba}}$$

and

$$\frac{\%\ Ba}{N_{Ba} \times 137.36} = \frac{\%\ Cl}{70.914 \times N_{MCl_2}}$$

$$\%\ Ba = \frac{N_{Ba} \times 137.36 \times \%\ Cl}{70.914 \times N_{MCl_2}} \qquad \text{(equation 13)}$$

These two equations require the knowledge of N_{Ba} and N_{Ca} as a function of N_{MCl_2}. This was obtained by drawing a tie-line on the ternary diagram from the salt composition through the initial overall composition to the calcium-barium binary boundary. N_{Ba} and N_{Ca} could be determined from this line for any value of N_{MCl_2}. Equations 12 and 13 were solved with different values of N_{MCl_2} with the corresponding values of N_{Ca} and N_{Ba} until the calculated analysis of the metal phase was successively approximated to be 100 percent. These values of calcium and barium were then taken as the composition of the metal phase.