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Solubilities of Bromide Salts of Aluminum, Cobalt, Lead, Manganese, Potassium, and Sodium When Sparged With Hydrogen Bromide

By E. G. Noble and D. E. Shanks

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UNITED STATES DEPARTMENT OF THE INTERIOR



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**UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mm	millimeter
g	gram	μm	micrometer
h	hour	pct	weight percent
L	liter	psig	pound (force) per square inch, gauge
mL	milliliter		
mL/min	milliliter per minute		

SOLUBILITIES OF BROMIDE SALTS OF ALUMINUM, COBALT, LEAD, MANGANESE, POTASSIUM, AND SODIUM WHEN SPARGED WITH HYDROGEN BROMIDE

By E. G. Noble¹ and D. E. Shanks²

ABSTRACT

The effects of HBr concentration and temperature on the solubility and hydration state of AlBr_3 , CoBr_2 , PbBr_2 , MnBr_2 , KBr , and NaBr were investigated by the Bureau of Mines. Saturated aqueous solutions of the Al, Pb, K, and Na bromides were sparged with HBr gas at 20°, 40°, and 60° C, and saturated solutions of Co and Mn bromides were sparged at 20° C. Increased HBr concentration caused decreased salt solubility because of the common ion effect for all the investigated bromides except PbBr_2 . Aqueous solubilities at 20° C were, in percent, 51.7 for AlBr_3 , 53.2 for CoBr_2 , 1.1 for PbBr_2 , 59.6 for MnBr_2 , 39.5 for KBr , and 47.4 for NaBr . At 60° C, the solubilities were, in percent, 53.3 for AlBr_3 , 2.2 for PbBr_2 , 46.0 for KBr , and 53.8 for NaBr . Solubilities in solutions sparged to HBr saturation at 20° C were, in percent, 0.5 for AlBr_3 , 42.0 for CoBr_2 , 32.2 for PbBr_2 , 21.0 for MnBr_2 , 0.6 for KBr , and 0.3 for NaBr . At 60° C, the solubilities at HBr saturation were, in percent, 1.8 for AlBr_3 , 41.4 for PbBr_2 , 1.3 for KBr , and 0.4 for NaBr . CoBr_2 precipitated out to a minimum solubility of 27.2 pct at 28.7-pct-HBr concentration. Further increases in HBr concentration increased CoBr_2 solubility because of the formation of bromide complexes. PbBr_2 increased in solubility as HBr concentration increased.

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INTRODUCTION

Many hydrometallurgical processes make use of acid halide systems. Most of the metal chlorides are highly soluble in an aqueous solution, but many can be removed from solution by increasing the chloride ion activity. A decrease in solubility of the metal chloride results from the common ion effect. Practical use of the sensitivity of chloride salt solubility to changes in HCl concentration can significantly improve the efficiency of chloride hydrometallurgical processes. Less work has been done with metal bromides; it is not known whether they always behave in an analogous manner to their chloride counterparts.

The Bureau of Mines has previously studied the effect of sparging crystallization with HCl gas on aqueous metal chlorides. Solubility and crystal composition data were obtained to aid in designing separations and purifications in chloride metallurgical systems. Data available in the literature were insufficient for this purpose. The Bureau has collected and published data on transition metal chloride systems (1)³ and alkali and alkaline earth metal chloride systems (2). The Bureau's HCl process for producing alumina from clay makes use of solubility differences in the $\text{AlCl}_3\text{-HCl-H}_2\text{O}$ system (3). Crystalline aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) of sufficient purity to meet aluminum industry standards is recovered from impure pregnant liquor by the decrease in solubility that results with the addition of HCl gas.

Some metal chloride mixtures cannot be separated on the basis of their solubility differences in the metal chloride-HCl-H₂O systems. An examination of published metal bromide solubility data indicated greater metal solubilities of some metal bromide-HBr-H₂O systems

compared with the corresponding metal chloride-HCl-H₂O systems. This could have significance especially in systems where high metal salt loadings are desirable. Bromide reagents are more costly than chloride reagents, but recycling the reagents, as is typically done in metallurgical processes, would minimize the difference.

The goals of this research were to obtain solubility and crystal composition data for the bromides of Al, Co, Pb, Mn, K, and Na in metal bromide-HBr-H₂O systems, to determine whether the bromides differed significantly from the corresponding chloride systems, and to determine if the findings could be used to develop new metal separation schemes. There are few bromide solubility data available in the literature.

Some aqueous solubility data are available for Co, Pb, Mn, K, and Na bromides, but none exist for AlBr_3 . Linke (4) summarized the relevant publications prior to 1957. However, of these, only Scott and Durham (5) reported solubility data for metal bromide-HBr-H₂O systems. Their data for KBr and NaBr systems were the only data of interest to this research. Scott and Durham used long-term equilibrium tests at 25° C using closed containers and predetermined amounts of constituents. A survey of post-1956 literature showed results of metal bromide solubility studies only for mixed salt systems or nonaqueous solutions.

In this research, the metal bromide-HBr-H₂O systems were studied at 20°, 40°, and 60° C. These temperatures were used so the data could be compared with those obtained from the Bureau's metal chloride studies. The $\text{CrBr}_2\text{-HBr-H}_2\text{O}$ system was investigated, but equilibrium was too slow to produce valid data from sparging crystallization. The other bromides exhibited rapid equilibria, as had their chloride analogues.

³Underlined numbers in parentheses refer to items in the list of references preceding appendix A.

MATERIALS AND EQUIPMENT

Sparging was performed in either a 1-L or a 3-L water-jacketed borosilicate glass resin reaction kettle with a four-port lid (fig. 1). The 1-L kettle was used for the Al, Co, Pb, and Mn salts. Potassium and sodium bromides were studied in the 3-L kettle. Temperature was monitored with a mercury thermometer marked in 0.1°C increments. The circulator bath, pressure regulators, flow meters, and stirring apparatus have been described previously (1).

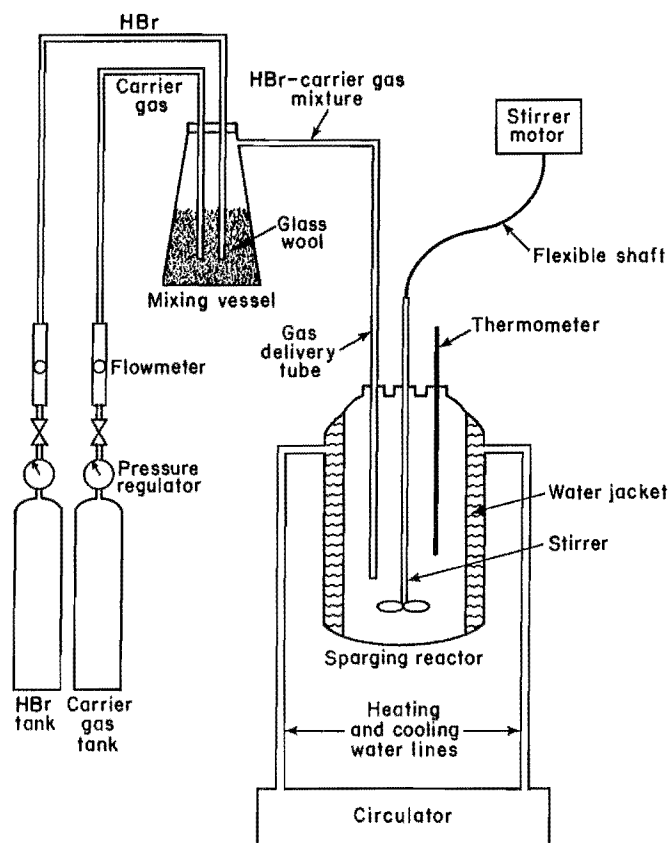


FIGURE 1.—Sparging apparatus.

Each experiment started with a saturated aqueous solution of the metal bromide salt. Reagent-grade KBr and NaBr were used, and the other bromides were of the purest grade available: AlBr_3 , 99.997 pct; $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$, purified; $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, unspecified purity; and PbBr_2 , 98+ pct. A near-saturated aqueous solution of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ contained fines that were not water soluble. The solution was filtered through a fluorocarbon polymer $5.0\text{-}\mu\text{m}$ membrane filter to remove the fines. The filtrate was heated to evaporate enough water to obtain a saturated solution. The sparging gas was HBr with a minimum purity of 99.8 pct (impurity: HCl, maximum 0.20 pct). Reagents used for analytical purposes were 0.1000N HCl [standardized at 25°C against 2-amino-2-(hydroxymethyl)-1, 3-propanediol (TRIS)]; 0.1000N NaOH (standardized at 25°C against potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$)); AgNO_3 , reagent grade; and dipotassium oxalate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$), reagent grade.

Crystal-free samples of solution were removed from the reaction kettle through a coarse-porosity, fritted-glass gas-dispersion tube, 250 mm long with an 8-mm-diam stem and a 12-mm-diam cylindrical disk. Hydrogen ion and total bromide ion concentrations were determined with an automatic titrating apparatus with a standard pH electrode for hydrogen ion titrations and a bromide-ion-specific electrode for bromide titrations. Reference electrodes were sleeve, double-junction, calomel-internal, with a salt bridge filling solution of sodium acetate-sodium nitrate ($\text{NaC}_2\text{H}_3\text{O}_2\text{-NaNO}_3$). Aliquots of the diluted samples in the volumetric flasks were drawn with a 1-mL automatic pipet with $\pm 0.6\text{-pct}$ accuracy.

PROCEDURE

Approximately 800mL of saturated bromide solution was prepared for the 1-L kettle and approximately 2,500 mL for the 3-L kettle. Saturated solutions were prepared by heating an appropriate amount of water to slightly higher than the desired temperature, slowly stirring in the bromide until excess solids remained for at least 24 h after the last addition, and cooling to the desired temperature. Special precautions were taken in preparing the AlBr_3 solutions because of AlBr_3 's property of violent hydrolysis in water. However, this violent reaction decreased as the concentration of salt in solution increased. The salt was initially dissolved in a minimum amount of water in a Pyrex⁴ glass beaker large enough to contain the spatters. When the initial amount of water became saturated, additional water was added, and saturation was slowly achieved again. Preparation of the solution continued in this manner until the desired volume was reached. The PbBr_2 solutions were prepared with a large excess of solids present to allow for dissolution as the acid concentration rose during sparging.

The solutions were maintained at 20°, 40°, or 60° C and sparged with a mixture of HBr and N_2 carrier gas until saturated with HBr. The HBr passing through the flowmeter was regulated at 10 psig and adjusted to a flow rate of 150 mL/min in the 1-L kettles and 350 mL/min in the 3-L kettles. The carrier gas was regulated at 10 psig and delivered at a flow rate of 200 mL/min through the flowmeter. The stirrer speed was adjusted to the minimum speed that would keep the solids in suspension. The HBr flow rate was chosen to give a reasonable sampling frequency and allow adequate monitoring of possible hydration changes. The bromide salt solution was sampled prior to sparging and hourly until the conclusion of the experiment. Approximately 5-mL samples

were drawn from the slurry through a fritted-glass gas-dispersion tube to insure that no solids were removed. The sample was added to a 100-mL volumetric flask approximately half full of a weighed amount of water. The volumetric flask was weighed after the sample was added and again after the flask was filled to the 100-mL mark. This minimized loss of HBr by vaporization and allowed calculation of the weight of the sample and the density of the diluted sample. Specific gravity was determined on solutions separated from 20° C slurries with a Mettler-Parr DMA 35 specific gravity meter with ± 0.001 accuracy. Since this instrument can only be used in the 10° to 30° C range, the specific gravity of the 40° and 60° C solutions was determined by weighing a 5-mL sample of the solution. The results obtained by weighing a known volume showed considerable scatter and varied by as much as ± 3 pct; therefore, the specific gravity values reported in tables B-1, B-3, B-5, and B-6 at 40° and 60° C were determined from smoothed curves. To obtain residue samples, approximately 5 mL of slurry was collected with a ladle. The slurries were partially deliquored by blotting on glass-fiber filter paper and were then added to tared volumetric flasks half full of water. They were further processed in the same manner as the liquid samples.

Diluted samples were prepared for analysis by pipeting 1-mL aliquots from the volumetric flasks. To assure accurate results, the aliquot was weighed and its weight divided by the solution density. The HBr concentration was determined by titrating the 1-mL aliquot, diluted to 50 mL with water or, in the case of the AlBr_3 and PbBr_2 samples, a 5-pct aqueous solution of dipotassium oxalate, with standardized 0.1000N NaOH. Dipotassium oxalate forms complexes with those cations that interfere with the potentiometric titration of free acid in salt solutions (6). The automatic titrator determined the endpoint of the reaction as the point of maximum rate of change in

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

the first derivative of the titration curve and printed out the volume of titrant consumed in reaching the endpoint. HBr concentration was calculated from equation A-1, which is shown in appendix A.

Metal bromide concentration, for all salts except PbBr_2 , was determined by titrating a weighed 1-mL aliquot, diluted to 50 mL with water, with standardized 0.100N AgNO_3 and detecting the change in bromide concentration with a bromide-specific-ion electrode. The endpoint volume was converted to metal bromide concentration by equation A-2.

Metal bromide concentration was checked by a gravimetric technique, for all bromides except AlBr_3 , in which 25-mL aliquots were dried under heat lamps, heated to 200° C in a muffle furnace, cooled in a vacuum desiccator, and weighed as an anhydrous metal bromide. AlBr_3 concentration was confirmed by atomic absorption (AA) analysis. Inductively coupled plasma (ICP) analysis on low AlBr_3 and PbBr_2 concentrations was

used to supplement the results obtained by other methods.

Analysis of PbBr_2 solutions required special procedures because of the low solubility of PbBr_2 in water. ICP analysis was used to analyze PbBr_2 in 0 to 15 pct HBr solutions. The results were checked against gravimetric results obtained as described above. Above approximately 15-pct HBr, the 5-mL samples removed from the reaction kettle precipitated when diluted with water in the volumetric flasks. Gravimetric analysis was performed on the total volume of the mixture in the flask, including the precipitate, less 1 mL removed for HBr analysis.

The experiments were terminated when HBr sparging ceased to influence the HBr and bromide salt concentrations. The wet residue and solution compositions were plotted on triangular coordinates, and tielines were constructed to determine crystal composition by Schreinemaker's wet residue method (7).

RESULTS AND DISCUSSION

The Al, Co, Mn, K, and Na bromide systems exhibited solubilities that were similar to those of the analogous metal chloride systems (1-3). Thus, the data indicate that the use of the bromides of these metals would not result in improved metallurgical separations. However, the PbBr_2 solubility data show significantly greater loading capacity in concentrated HBr than has been reported for PbCl_2 in concentrated HCl (8). This behavior has possible process application.

The metal bromides that were studied at 20°, 40°, and 60° C showed a slight increase in aqueous solubility with increased temperature. All bromides, except PbBr_2 , decreased in solubility as HBr concentration increased, because of the common ion effect. CoBr_2 solubility increased at high HBr concentrations because complexes form at sufficiently high bromide ion concentration. PbBr_2 , which is almost insoluble in water, increased in solubility as the HBr concentration increased. The formation

of PbBr_2 complexes with increasing bromide ion concentration was more important than the common ion effect.

The only solubility data in the literature for metal bromide-HBr- H_2O systems are for the KBr and NaBr systems, and none of these data were obtained at 20°, 40°, or 60° C. However, the solubilities of the KBr and NaBr systems do not vary significantly with increased temperature. The 20° C data obtained for KBr and NaBr in this investigation compare closely with the literature data for these systems at 25° C (5). The results confirmed that rapid equilibrium is attained in these systems with HBr-sparging crystallization.

Insufficient quantities of purified CoBr_2 and MnBr_2 prevented the study of these metal bromides at 40° and 60° C. Initial investigations showed that the presence of even small amounts of impurities interfered with complete crystallization of the salt at high HBr concentrations, i.e., the purer the metal bromide

reagent, the more HBr the system could absorb.

Data for the six systems at the temperature ranges investigated are summarized in tables B-1 to B-6 in appendix B. The metal bromide data in each table represent a composite of analyses from the several analytical procedures used. From these tabulations, the solubility curves in figures 2, 6, 8, 10, 11, and 15 and the tieline diagrams in figures 3, 4, 5, 7, 9, 12, 13, and 14 were plotted. Since KBr and PbBr_2 do not form hydrates (4), wet residues from their HBr- H_2O system were not analyzed. Specific gravity data are included in the tables for general information, but were not an integral part of the solubility studies.

ALUMINUM BROMIDE

No literature solubility data were available for AlBr_3 , but this bromide was expected to behave much like the corresponding chloride system in which AlCl_3 exists as the hexahydrate at 20°, 40°, and 60° C, and AlCl_3 solubility does not significantly change with temperature (3). AlBr_3 readily hydrolyzes in water, and the "CRC Handbook of Chemistry and Physics" (9) indicates that it can exist

in the anhydrous, hexahydrate, and pentadecahydrate forms.

AlBr_3 concentration as a function of HBr concentration at 20° C is tabulated in table B-1 and plotted in figures 2 and 3. AlBr_3 solubility decreased from 51.7 pct in water to 0.5 pct in 61.0-pct HBr. Between 29.7- and 30.5-pct HBr, physical observations and chemical analysis indicated a phase change. Despite continued sparging of HBr into the system between sampling, there were three almost identical AlBr_3 solubility and HBr concentration points (fig. 2), and a decrease in crystal size and settling time of the crystals. Both behaviors typically signal a phase change. Because of the highly deliquescent nature of the crystals, it was not possible to measure any differences in size or observe any changes in shape. The crystals were colorless before and after the indicated phase change. The wet residue composition changed, and the tieline plot (fig. 3) shows a shift to the hexahydrate from a more hydrated species. The tielines for solution concentrations less than 30-pct HBr intersect the 0-pct-HBr line close to the nonhydrate composition. This hydrate is not described in the literature and is difficult to confirm.

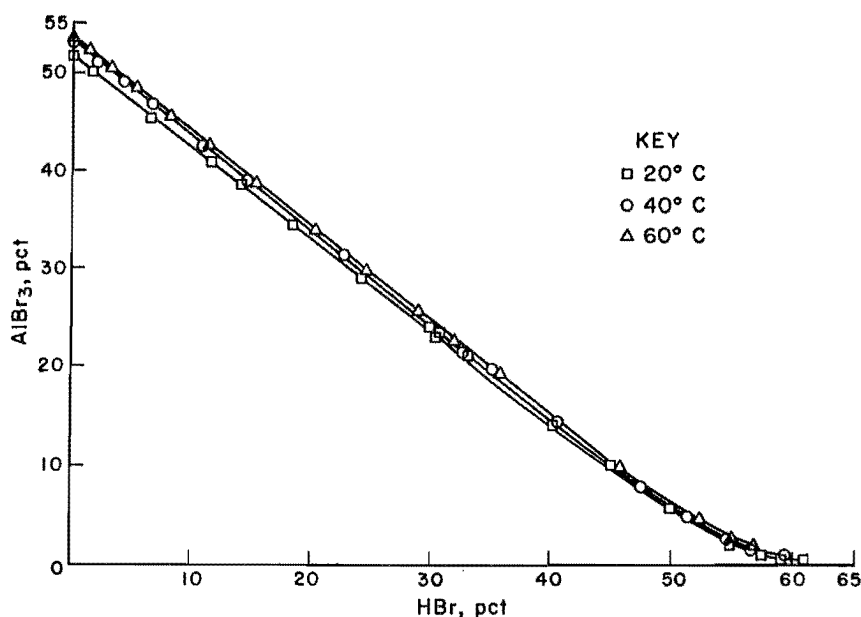


FIGURE 2.—Solubility of AlBr_3 as function of HBr concentration and temperature in the AlBr_3 -HBr- H_2O system.

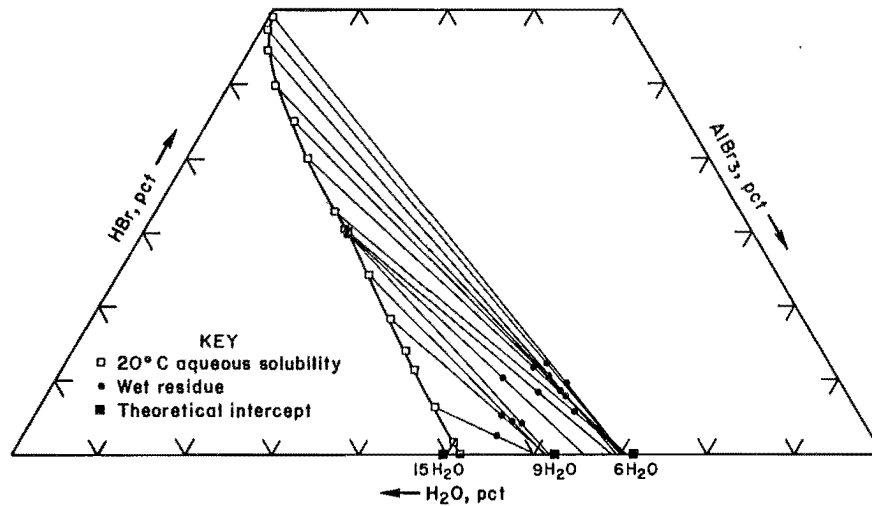


FIGURE 3.—Tie-line plot of data for the $\text{AlBr}_3\text{-HBr-H}_2\text{O}$ system at 20°C .

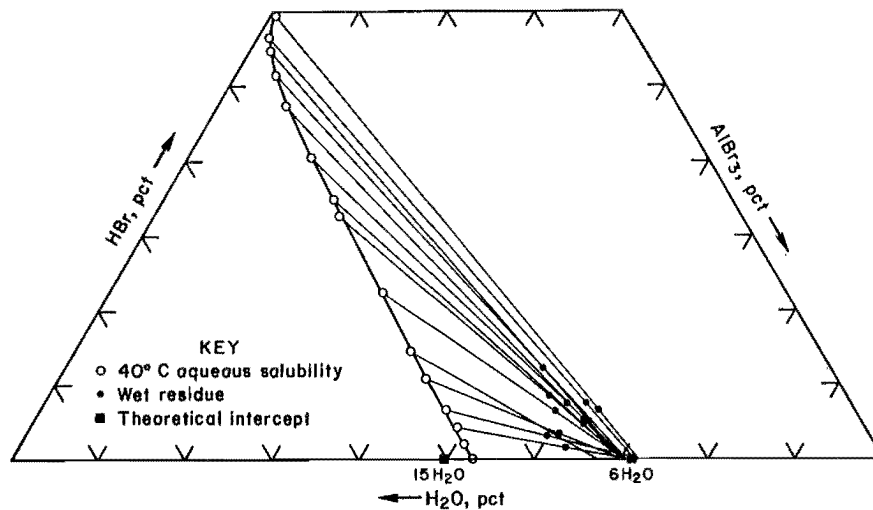


FIGURE 4.—Tie-line plot of data for the $\text{AlBr}_3\text{-HBr-H}_2\text{O}$ system at 40°C .

X-ray diffraction analysis could not confirm the composition because of insufficient published patterns.

AlBr_3 concentration as a function of HBr concentration at 40°C is tabulated in table B-1 and plotted in figures 2 and 4. AlBr_3 solubility decreased from 53.0 pct in water to 0.9 pct at 59.2-pct HBr . No indications of a phase change were observed during sparging, and the tie-line plot (fig. 4) confirms that the hexahydrate was present throughout the study.

AlBr_3 concentration as a function of HBr concentration at 60°C is tabulated

in table B-1 and plotted in figures 2 and 5. The solubility of AlBr_3 ranged from 53.4 pct in water to 1.8 pct at HBr saturation (56.8 pct). The tie-line plot indicates that solid AlBr_3 was present only as the hexahydrate at this temperature.

COBALT BROMIDE

CoBr_2 concentration as a function of HBr concentration at 20°C is tabulated in table B-2 and plotted in figures 6 and 7. Aqueous solubility was 53.2 pct. Linke reported CoBr_2 solubility at 25°C

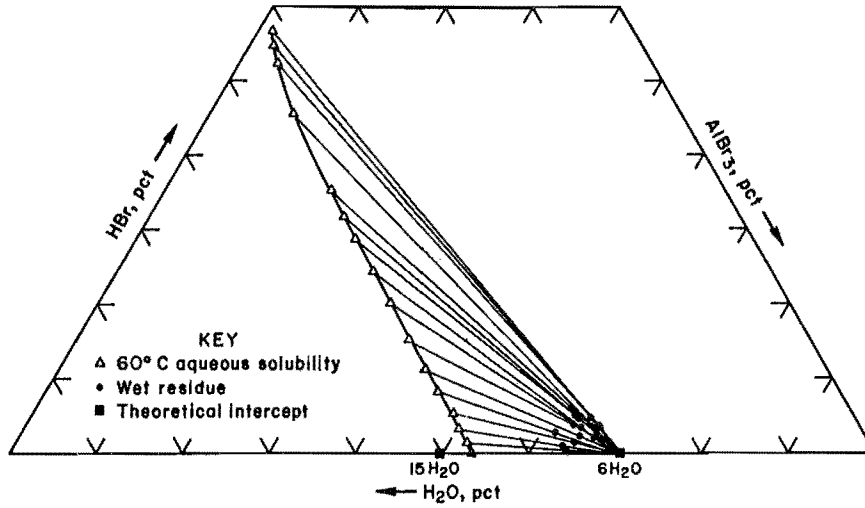


FIGURE 5.—Tie-line plot of data for the $\text{AlBr}_3\text{-HBr-H}_2\text{O}$ system at 60°C .

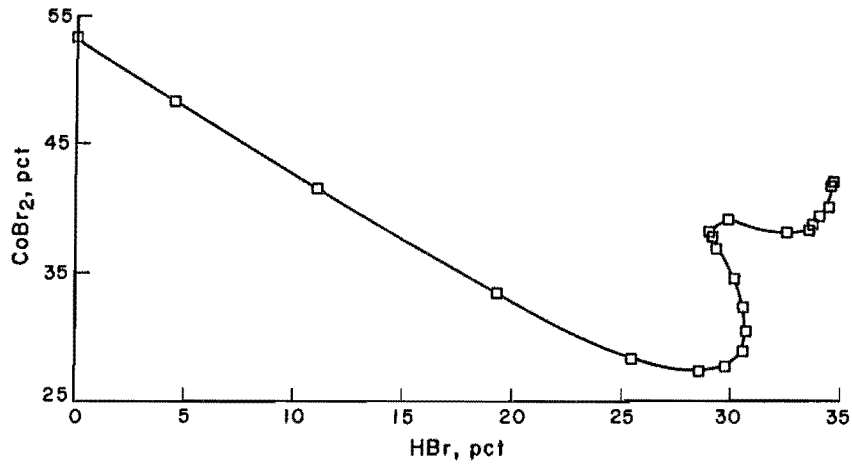


FIGURE 6.—Solubility of CoBr_2 as function of HBr concentration at 20°C in the $\text{CoBr}_2\text{-HBr-H}_2\text{O}$ system.

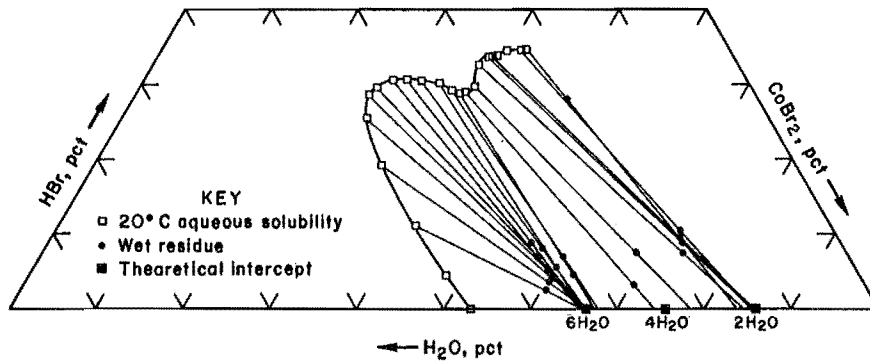


FIGURE 7.—Tie-line plot of data for the $\text{CoBr}_2\text{-HBr-H}_2\text{O}$ system at 20°C .

to be 54.4 pct (4). Minimum CoBr_2 solubility was 27.2 pct at 28.6-pct HBr. As sparging continued, the HBr content of the solution increased to 30.7 pct, and then decreased to 29.0 pct as the CoBr_2 content of the solution increased to 37.4 pct. During these changes, the solution and the crystals turned from red-purple to blue-violet. The tieline plot (fig. 7) shows the transition from the hexahydrate to the dihydrate where the solution composition was 29.9-pct HBr and 38.9-pct CoBr_2 . In the $\text{CoCl}_2\text{-HCl-H}_2\text{O}$ system at 20° C, a similar gradual transition from the hexahydrate to the dihydrate form occurred (1). A second CoBr_2 solubility minimum was found at 32.5-pct HBr, 37.9-pct CoBr_2 . CoBr_2 solubility increased to 42.2 pct at HBr saturation (35.1 pct).

LEAD BROMIDE

Solubility data for PbBr_2 are not available in the literature. PbBr_2 concentration as a function of HBr concentration at 20°, 40°, and 60° C is tabulated in table B-3 and plotted in figure 8. Since PbBr_2 does not form hydrates, no residue samples were analyzed. At 20° C, PbBr_2 aqueous solubility was 1.1 pct. Minimum solubility was 0.2 pct at 5.0-pct HBr; maximum solubility was 39.9 pct at 29.7-pct HBr. At HBr saturation (43.6 pct), PbBr_2 solubility was 32.2 pct. The results at 40° and 60° C were similar. PbBr_2 solubility in water at 40° C was 1.4 pct; at HBr saturation (37.7 pct), it was 36.4 pct. Minimum PbBr_2 solubility was 0.5 pct at 4.3-pct HBr; maximum solubility was 41.4 pct at 29.3-pct HBr. At 60° C, PbBr_2 solubility ranged from 2.2 pct in water to 41.4 pct at HBr saturation

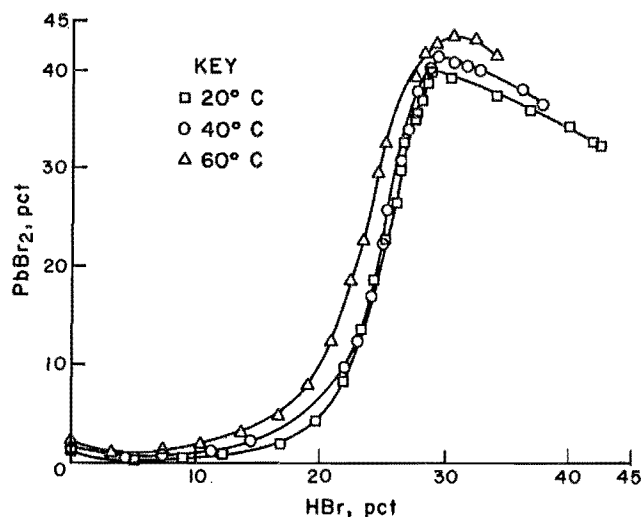


FIGURE 8.—Solubility of PbBr_2 as function of HBr concentration and temperature in the $\text{PbBr}_2\text{-HBr-H}_2\text{O}$ system.

(34.0 pct). The solubility minimum was 1.1 pct at 3.2-pct HBr, and the maximum was 43.4 pct at 30.6-pct HBr.

MANGANESE BROMIDE

Linke reported MnBr_2 aqueous solubility at 20° C to be 59.5 pct and the solid phase as the tetrahydrate. MnBr_2 concentration as a function of HBr concentration at 20° C is tabulated in table B-4 and plotted in figures 9 and 10. Solubility in water was 59.6 pct and 21.0 pct at HBr saturation (47.2 pct). MnBr_2 solubility minimums occurred at 35.9 pct HBr (23.3 pct MnBr_2) and 45.4 pct HBr (20.4 pct MnBr_2). The invariant point was at 37.1 pct HBr, 26.1 pct MnBr_2 . The tieline plot, figure 10, confirms that the solid phase changed from the tetrahydrate to the dihydrate at this composition.

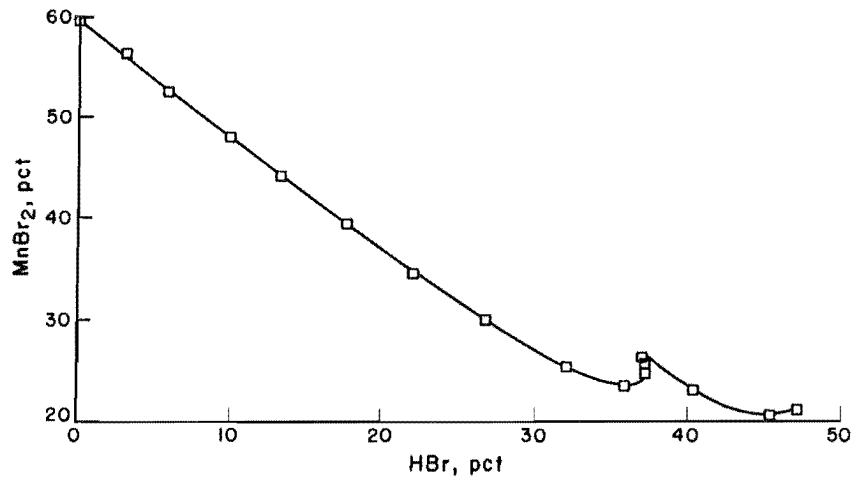


FIGURE 9.—Solubility of MnBr_2 as function of HBr concentration at 20°C in the MnBr_2 -HBr- H_2O system.

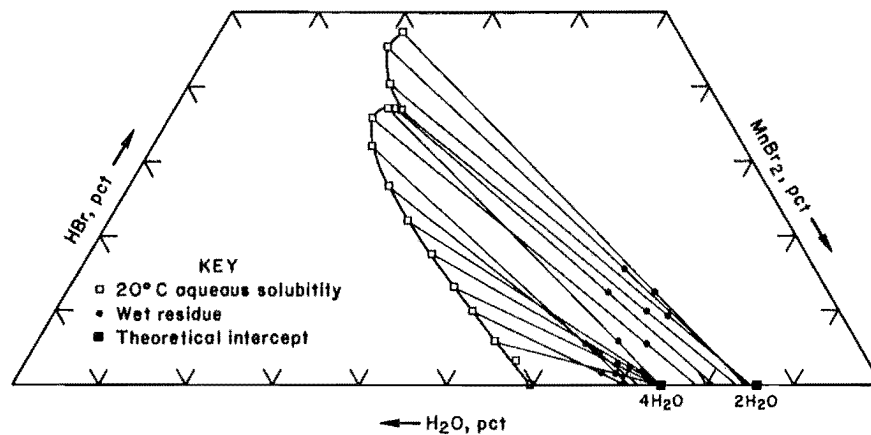


FIGURE 10.—Tie-line plot of data for the MnBr_2 -HBr- H_2O system at 20°C .

POTASSIUM BROMIDE

KBr concentration as a function of HBr concentration at 20° , 40° , and 60°C is tabulated in table B-5 and plotted in figure 11. The solubility curves in figure 11 are similar to those obtained for the KCl - HCl - H_2O system (2) and like KCl , KBr precipitated out almost completely when acid was at saturation levels. Residues were not analyzed because KBr does not form hydrates.

At 20°C , aqueous KBr solubility was 39.5 pct; Linke reported 39.4 pct. At HBr saturation (57.8 pct), KBr solubility was 0.4 pct. KBr solubility at 40°C

ranged from 43.0 pct in water (Linke reported 43.2 pct) to 0.8 pct at HBr saturation (58.4 pct). At 60°C , a similar solubility increase was observed; KBr solubility was 46.0 pct in water and 1.3 pct at HBr saturation (56.9 pct). Linke reported 60°C aqueous solubility as 46.1 pct.

SODIUM BROMIDE

Unlike NaCl , NaBr exists as a dihydrated salt in water at temperatures below the 50° to 60°C range. Near HBr saturation, NaBr salting out is almost complete; this also occurs in the NaCl - HCl - H_2O system (2). The NaBr -HBr- H_2O

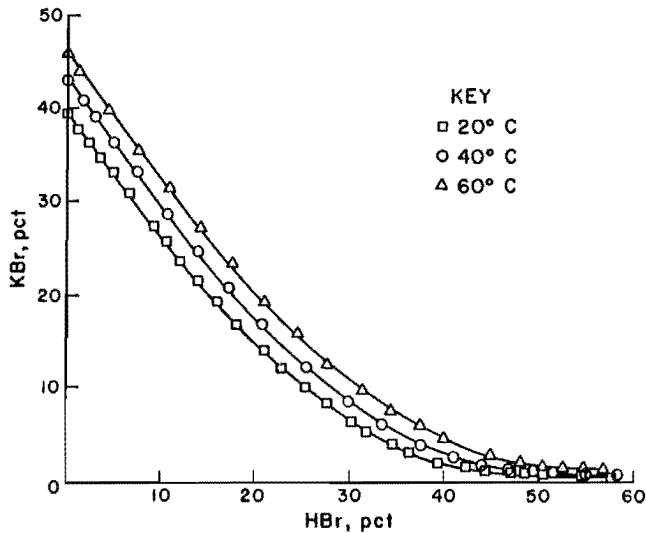


FIGURE 11.—Solubility of KBr as function of HBr concentration and temperature in the KBr-HBr-H₂O system.

system is slightly more temperature dependent than the NaCl-HCl-H₂O system.

NaBr concentration as a function of HBr concentration at 20° C is tabulated in table B-6 and plotted in figures 12 and 13. Aqueous NaBr solubility was 47.4 pct; Linke reported 47.6 pct. A slight invariant point occurred at 40.1-pct HBr, 7.0-pct NaBr (fig. 12). The tieline plot (fig. 13) confirmed the phase change at this concentration from the dihydrate to the anhydrous state. Minimum NaBr solubility, 0.3 pct, occurred at HBr saturation (59.3 pct).

No literature value is available for NaBr aqueous solubility at 40° C. NaBr concentration as a function of HBr concentration at 40° C is tabulated in table B-6 and plotted in figures 12 and 14. In water, NaBr solubility was 51.4 pct. The phase change from the dihydrate to

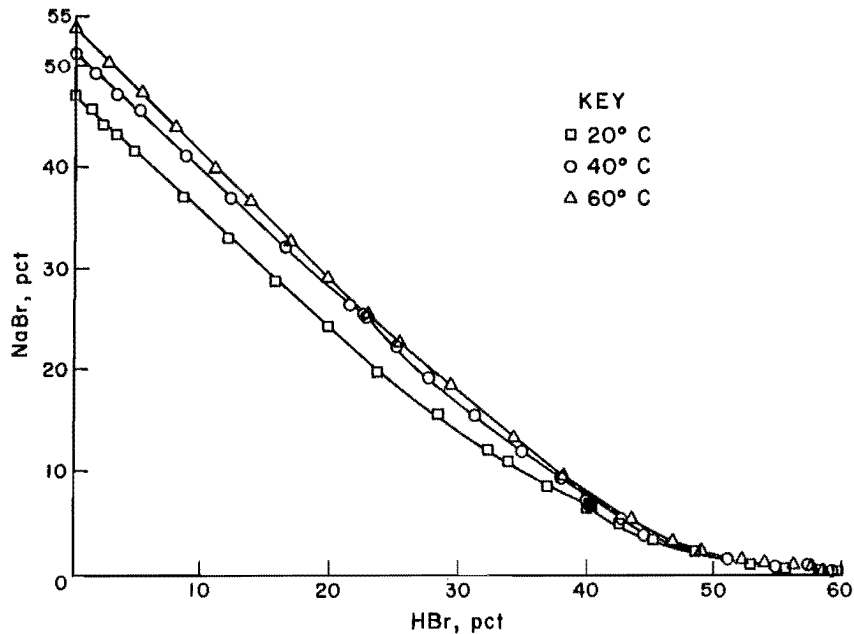


FIGURE 12.—Solubility of NaBr as function of HBr concentration and temperature in the NaBr-HBr-H₂O system.

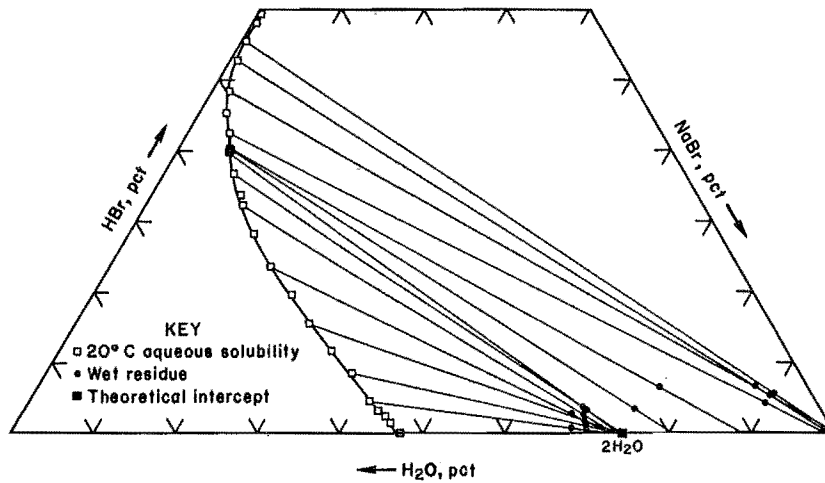


FIGURE 13.—Tie-line plot of data for the NaBr-HBr-H₂O system at 20° C.

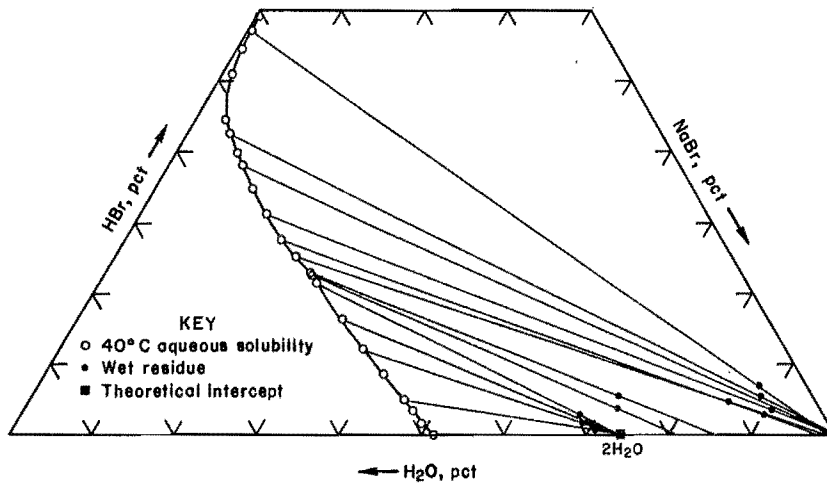


FIGURE 14.—Tie-line plot of data for the NaBr-HBr-H₂O system at 40° C.

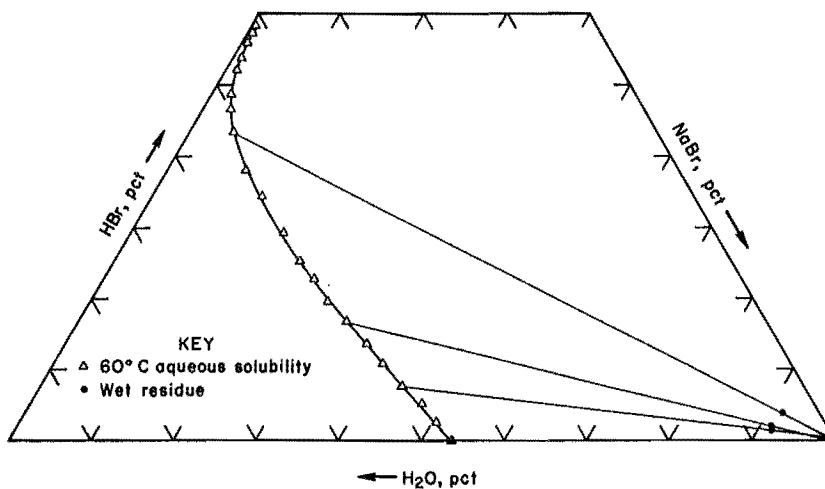


FIGURE 15.—Tie-line plot of data for the NaBr-HBr-H₂O system at 60° C.

the anhydride was indicated by the invariant point at 25.1-pct HBr, 22.3-pct NaBr on the solubility curve (fig. 12) and confirmed by the tieline plot (fig. 14). At HBr saturation (59.0 pct), NaBr was at minimum solubility, 0.4 pct.

NaBr concentration as a function of HBr concentration at 60° C is tabulated in table B-6 and plotted in figures 12 and

15. Aqueous NaBr solubility was 53.8 pct. Linke reported a value of 54.1 pct at 60° C. No phase change was indicated by the solubility curve (fig. 12), and the tieline data showed that solid NaBr is anhydrous at 60° C. At HBr saturation (58.3 pct), NaBr solubility was at the minimum, 0.4 pct.

SUMMARY AND CONCLUSIONS

Solubility data from HBr sparging of saturated solutions of AlBr_3 , CoBr_2 , PbBr_2 , MnBr_2 , KBr , and NaBr were obtained. Where literature values from conventional solubility equilibrium tests are available, the results agree. This agreement shows that solubility data obtained using the sparging crystallization method are as valid as the data obtained using the slower bottle-test methods.

Bromides of Al, Mn, K, and Na decreased in solubility and crystallized out of solution when sparged with HBr gas because of the common ion effect. The crystallization was almost total for Al, K, and Na bromides. CoBr_2 solubility initially decreased and then increased at high HBr concentration because of the formation of bromide complexes. PbBr_2 was almost insoluble in water and at low HBr concentrations. At high HBr concentrations, PbBr_2 solubility increased forty-fold, before decreasing slightly as HBr saturation was attained. In saturated HBr, the saturation composition of the metal bromides studied were as follows, in percent:

	20° C	40° C	60° C
AlBr_3	0.5	0.9	1.8
CoBr_2	42.0	NA	NA
PbBr_2	32.2	36.4	41.4
MnBr_2	21.0	NA	NA
KBr6	.8	1.3
NaBr3	.4	.4

NA Not analyzed.

The bromides of Pb and K were anhydrous. AlBr_3 formed the hexahydrate in saturated aqueous solutions at 40° and 60° C. At 20° C, the aqueous hydrated state could not be confirmed, but the tieline plot indicated the nonhydrate. Above 30-pct HBr, the hexahydrate was present. CoBr_2 was present as the hexahydrate in aqueous solutions at 20° C and formed the dihydrate above 31-pct HBr. MnBr_2 crystals at 20° C were the tetrahydrate in aqueous solutions and in solutions with HBr concentrations below 37.1 pct. At higher HBr concentrations, the dihydrate was formed. At 20° and 40° C, NaBr formed the dihydrate in aqueous solutions; while at 60° C, NaBr was anhydrous. At 20° C, NaBr changed to the anhydrous form at 40.1-pct HBr; at 40° C, the transition to anhydrous NaBr was at 25.1-pct HBr.

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APPENDIX A

A-1. - Equation for calculating HBr concentration

$$R_1 = E_1 \times C_1 \times C_2 / C_3 \times C_4$$

where

R_1 = concentration of HBr, pct,

E_1 = NaOH volume, mL,

C_1 = 809.2 = milliequivalent weight of HBr
 × volumetric flask volume × conversion factor for weight fraction to (weight) percent g,

C_2 = 0.1000 = NaOH concentration, N

C_3 = volume of aliquot titrated, mL,

and

C_4 = weight of sample taken from crystallizer, g.

A-2. - Equation for calculating metal bromide concentration

$$R_2 = [(E_2 \times C_6 / C_7) - R_3] (C_5 / C_4)$$

where R_2 = metal bromide concentration, pct,

E_2 = AgNO₃ volume, mL,

C_5 = milliequivalent weight metal bromide
 × volumetric flask volume × conversion factor for weight fraction to (weight) percent, g, (888.98 for AlBr₃, 1,093.8 for CoBr₂, 1,073.8 for MnBr₂, 1,190.0 for KBr, and 1,028.9 for NaBr),

C_6 = AgNO₃ concentration, N ,

C_7 = volume of aliquot titrated with AgNO₃, mL,

and

R_3 = correction for bromide contributed by HBr = $E_1 \times C_2 / C_3$.

APPENDIX B

TABLE B-1. - AlBr₃-HBr-H₂O system

Solution			Wet residue		Solution			Wet residue		Solution			Wet residue	
HBr, pct	AlBr ₃ , pct	sp gr	HBr, pct	AlBr ₃ , pct	HBr, pct	AlBr ₃ , pct	sp gr	HBr, pct	AlBr ₃ , pct	HBr, pct	AlBr ₃ , pct	sp gr	HBr, pct	AlBr ₃ , pct
20° C					40° C					60° C				
0	51.7	1.75	NA	NA	0	53.0	1.76	NA	NA	0	53.3	1.77	NA	NA
1.6	50.0	1.74	NA	NA	2.0	51.1	1.75	NA	NA	1.5	52.1	1.76	0.7	64.0
6.5	45.4	1.73	2.7	54.3	4.3	49.0	1.75	1.4	62.9	3.3	50.3	1.75	1.1	63.3
11.5	40.7	1.72	NA	NA	6.7	46.7	1.74	3.1	60.0	5.4	48.4	1.74	1.7	64.6
14.0	38.4	1.71	NA	NA	10.8	42.3	1.72	3.2	61.4	8.1	45.4	1.73	2.9	61.6
18.3	34.4	1.70	5.1	53.8	14.5	38.8	1.71	3.3	61.1	11.4	42.5	1.72	2.3	64.6
24.2	29.0	1.68	4.5	55.5	22.6	31.3	1.69	6.4	59.1	15.3	38.5	1.71	3.8	63.1
29.7	23.9	1.67	4.3	56.8	32.5	21.3	1.67	8.4	57.5	20.3	33.9	1.70	2.2	66.3
30.5	23.1	1.67	10.2	51.2	34.9	19.6	1.66	4.6	63.3	24.5	29.8	1.69	3.6	64.1
30.3	23.3	1.67	8.3	56.3	40.3	14.3	1.64	7.5	60.0	28.8	25.5	1.68	4.7	63.4
32.9	20.9	1.66	5.9	61.6	47.3	8.0	1.63	5.3	63.2	31.9	22.6	1.67	5.2	62.8
40.1	14.0	1.64	11.7	54.0	51.3	4.9	1.63	12.1	55.0	35.8	19.2	1.66	6.1	61.8
44.9	9.9	1.63	8.6	58.6	54.5	2.5	1.64	5.0	63.9	45.8	9.8	1.64	3.7	65.6
49.9	5.6	1.63	7.9	59.7	56.5	1.3	1.65	7.6	62.2	52.4	4.4	1.64	3.5	66.5
54.7	2.1	1.64	10.6	56.6	59.2	.9	1.68	6.6	64.1	54.9	2.5	1.65	3.7	66.2
57.3	.8	1.65	12.3	55.2						56.8	1.8	1.66	4.9	64.8
59.0	.5	1.68	9.3	59.0										
61.0	.5	1.72	NA	NA										

NA Not analyzed.

TABLE B-2. - CoBr₂-HBr-H₂O system, 20° C

Solution			Wet residue		Solution			Wet residue	
HBr, pct	CoBr ₂ , pct	sp gr	HBr, pct	CoBr ₂ , pct	HBr, pct	CoBr ₂ , pct	sp gr	HBr, pct	CoBr ₂ , pct
0	53.2	1.82	NA	NA	29.3	36.7	1.92	7.0	60.2
4.5	48.1	1.78	NA	NA	29.0	37.4	1.92	4.7	62.8
11.1	41.3	1.74	2.6	60.5	29.1	37.9	1.95	3.1	70.3
19.3	33.2	1.70	3.8	60.2	29.9	38.9	2.00	7.5	68.6
25.5	28.2	1.69	4.0	60.6	32.5	37.9	2.03	7.5	73.7
28.6	27.2	1.71	5.3	59.3	33.6	38.1	2.07	8.9	63.0
29.8	27.5	1.73	6.9	57.3	33.7	38.5	2.09	9.4	72.2
30.6	28.8	1.77	6.7	58.1	34.0	39.1	2.12	NA	NA
30.7	30.4	1.80	8.9	55.7	34.5	39.9	2.16	NA	NA
30.5	32.1	1.84	8.0	57.1	34.6	41.6	2.22	10.3	71.9
30.1	34.3	1.89	5.7	60.3	34.7	42.0	2.23	28.1	50.0

NA Not analyzed.

TABLE B-3. - $\text{PbBr}_2\text{-HBr-H}_2\text{O}$ system (solution)

HBr, pct	PbBr_2 , pct	sp gr	HBr, pct	PbBr_2 , pct	sp gr	HBr, pct	PbBr_2 , pct	sp gr
20° C			40° C			60° C		
0	1.1	1.00	0	1.4	1.01	0	2.2	1.01
5.0	.2	1.04	4.3	.5	1.03	3.2	1.1	1.03
9.0	.4	1.07	7.4	.7	1.06	7.3	1.2	1.06
12.2	.7	1.10	11.2	1.2	1.09	10.4	1.8	1.08
16.8	1.8	1.15	14.4	2.2	1.20	13.7	3.0	1.11
19.7	4.3	1.21	21.9	9.8	1.28	16.7	4.7	1.17
21.8	8.3	1.29	22.9	12.4	1.36	19.0	7.8	1.23
23.3	13.5	1.38	24.1	16.9	1.46	20.8	12.4	1.32
24.2	18.5	1.48	24.9	22.2	1.56	22.4	18.6	1.45
25.1	22.6	1.57	25.3	25.7	1.63	23.4	22.6	1.54
26.1	26.4	1.67	26.4	30.6	1.78	24.6	29.4	1.70
26.2	29.8	1.76	26.9	33.9	1.87	25.1	32.6	1.78
26.5	32.7	1.85	27.7	37.8	2.01	27.5	39.2	2.05
27.4	35.0	1.94	28.7	40.2	2.11	28.3	41.7	2.16
27.6	35.7	1.96	29.3	41.4	2.16	29.1	42.6	2.20
28.0	37.0	2.01	30.6	40.7	2.20	30.6	43.4	2.33
28.5	38.8	2.09	31.6	40.3	2.21	32.3	43.0	2.35
28.6	39.9	2.16	32.7	39.9	2.24	34.0	41.4	2.36
30.4	39.2	2.18	36.1	37.9	2.27			
34.1	37.4	2.21	37.7	36.4	2.28			
36.8	35.9	2.24						
39.9	34.2	2.25						
41.8	32.6	2.26						
42.4	32.2	2.27						

TABLE B-4. - $\text{MnBr}_2\text{-HBr-H}_2\text{O}$ system, 20° C

Solution			Wet residue		Solution			Wet residue	
HBr, pct	MnBr_2 , pct	sp gr	HBr, pct	MnBr_2 , pct	HBr, pct	MnBr_2 , pct	sp gr	HBr, pct	MnBr_2 , pct
0	59.6	1.94	NA	NA	32.1	25.4	1.78	5.5	63.1
3.2	56.3	1.92	NA	NA	35.9	23.3	1.80	5.5	70.2
5.9	52.7	1.90	1.6	68.6	37.2	24.7	1.85	5.8	66.8
9.9	48.0	1.87	1.6	67.0	37.2	25.7	1.88	12.5	62.2
13.3	44.1	1.85	2.9	68.1	37.1	26.1	1.89	9.9	68.0
17.7	39.4	1.82	2.3	70.0	40.3	23.1	1.89	9.3	70.9
22.0	34.6	1.80	1.9	71.5	45.4	20.4	1.91	15.6	62.5
26.8	30.0	1.78	4.2	65.4	47.2	21.0	1.96	12.6	67.5

NA Not analyzed.

TABLE B-5. - KBr-HBr-H₂O system (solution)

HBr, pct	KBr, pct	sp gr	HBr, pct	KBr, pct	sp gr	HBr, pct	KBr, pct	sp gr
20° C			40° C			60° C		
0	39.5	1.37	0	43.0	1.39	0	46.0	1.43
1.3	37.7	1.36	1.5	40.8	1.38	1.4	44.0	1.42
2.3	36.3	1.36	2.8	39.1	1.37	4.4	39.8	1.40
3.6	34.7	1.35	4.9	36.4	1.36	7.7	35.5	1.39
4.9	33.2	1.35	7.4	33.2	1.35	10.9	31.5	1.37
6.7	31.0	1.34	10.7	28.7	1.34	14.2	27.3	1.36
9.2	27.4	1.33	13.9	24.7	1.33	17.6	23.5	1.35
10.6	25.8	1.33	17.2	21.1	1.32	21.0	19.4	1.34
12.0	23.8	1.32	20.6	16.9	1.32	24.3	16.0	1.34
14.0	21.7	1.32	25.4	12.4	1.32	27.7	12.6	1.35
16.0	19.5	1.32	29.9	8.7	1.34	31.3	9.8	1.36
18.1	17.0	1.31	33.5	6.2	1.36	34.4	7.5	1.38
21.0	14.1	1.31	37.5	4.0	1.38	37.4	5.9	1.40
22.8	12.3	1.32	40.9	2.7	1.41	40.0	4.7	1.42
25.4	10.0	1.32	43.9	1.9	1.44	44.9	2.8	1.47
27.6	8.3	1.33	46.8	1.3	1.48	48.0	2.1	1.50
30.2	6.4	1.34	49.5	1.1	1.52	50.4	1.7	1.53
31.9	5.2	1.35	51.6	.9	1.54	52.7	1.5	1.57
34.5	4.1	1.36	54.9	.8	1.59	54.8	1.4	1.59
36.3	3.2	1.38	58.4	.8	1.64	56.9	1.3	1.63
39.3	2.2	1.40						
42.3	1.5	1.43						
44.4	1.2	1.45						
47.1	1.0	1.48						
48.5	.8	1.50						
50.5	.7	1.53						
54.6	.6	1.60						
57.8	.6	1.65						

TABLE B-6. - NaBr-HBr-H₂O system

Solution			Wet residue		Solution			Wet residue		Solution			Wet residue	
HBr, pct	NaBr, pct	sp gr	HBr, pct	NaBr, pct	HBr, pct	NaBr, pct	sp gr	HBr, pct	NaBr, pct	HBr, pct	NaBr, pct	sp gr	HBr, pct	NaBr, pct
20° C					40° C					60° C				
0	47.4	1.53	NA	NA	0	51.4	1.58	NA	NA	0	53.8	1.61	NA	NA
1.3	45.8	1.53	NA	NA	1.6	49.3	1.57	NA	NA	2.7	50.4	1.59	NA	NA
2.2	44.4	1.52	NA	NA	3.3	47.4	1.56	NA	NA	5.2	47.3	1.57	NA	NA
3.2	43.3	1.52	NA	NA	5.0	45.5	1.55	0.7	70.8	7.8	43.9	1.55	1.2	91.4
4.6	41.7	1.51	0.8	67.8	8.6	41.2	1.54	NA	NA	10.9	39.9	1.54	NA	NA
8.4	37.2	1.50	1.1	69.3	12.1	37.0	1.52	1.7	68.8	13.8	36.5	1.53	NA	NA
11.8	33.2	1.48	NA	NA	16.4	32.3	1.51	1.9	69.1	16.9	32.6	1.52	2.0	91.0
15.6	28.8	1.47	1.7	68.5	21.5	26.5	1.49	2.9	67.8	19.7	28.9	1.51	NA	NA
19.7	24.3	1.46	NA	NA	22.6	25.5	1.48	3.9	71.9	22.8	25.4	1.50	NA	NA
23.7	19.9	1.45	2.7	66.8	22.7	25.4	1.48	5.6	71.2	25.3	22.6	1.50	NA	NA
28.2	15.5	1.45	NA	NA	25.1	22.3	1.46	4.7	84.8	29.3	18.5	1.49	NA	NA
32.1	12.0	1.45	2.8	68.2	27.7	19.2	1.46	2.9	90.0	34.3	13.4	1.49	NA	NA
33.7	11.0	1.45	NA	NA	31.2	15.5	1.47	3.3	90.8	38.1	9.5	1.48	NA	NA
36.8	8.6	1.46	3.2	68.1	34.9	11.9	1.47	NA	NA	43.5	5.4	1.49	3.8	91.5
39.7	6.6	1.48	3.6	67.7	38.0	9.1	1.47	2.1	94.7	46.7	3.2	1.51	NA	NA
40.0	6.8	1.48	3.4	74.0	39.8	7.4	1.48	NA	NA	48.9	2.2	1.53	NA	NA
40.1	6.7	1.48	6.5	75.6	42.7	5.3	1.49	5.2	88.2	52.1	1.2	1.56	NA	NA
42.4	5.1	1.49	4.2	89.4	44.4	3.8	1.49	NA	NA	53.9	1.0	1.59	NA	NA
45.1	3.5	1.50	NA	NA	50.9	1.5	1.54	NA	NA	56.0	.8	1.62	NA	NA
48.3	2.1	1.52	5.5	89.4	54.6	.7	1.60	NA	NA	57.6	.6	1.65	NA	NA
52.6	1.0	1.57	6.6	86.9	57.2	.5	1.64	6.9	87.2	58.3	.4	1.66	NA	NA
55.4	.5	1.62	5.4	88.7	59.0	.4	1.66	NA	NA					
58.0	.4	1.66	NA	NA										
59.3	.3	1.69	NA	NA										

NA Not analyzed.