

THE HIGH TEMPERATURE HYDROLYSIS
OF LITHIUM BROMIDE

By

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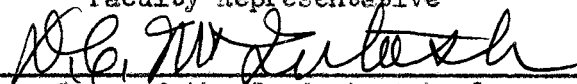
THESIS AND ABSTRACT APPROVED:



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273768

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Title of Study: The High Temperature Hydrolysis of Lithium Bromide

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Scope of Study: The possibility of the hydrolysis of molten halides at high temperatures has been suggested from time to time to explain the loss of halogen when such mixtures were heated for extended periods. Recently Briner and Roth have made an extensive study of the high temperature hydrolysis of alkali chlorides. These workers report considerable hydrolysis. The purpose of this study was to obtain some experimental data on the high temperature hydrolysis of alkali halides, and to analyze these data obtained with reference to thermochemical computations for the high temperature hydrolysis of the alkali halide salts.

Findings and Conclusions: It was found, in the case of lithium bromide, that the reaction does not proceed as a direct hydrolysis. The presence of even a small amount of oxygen in the reaction chamber results in a rapid liberation of free bromine, which increases with the introduction of water vapor. If the molten halide is allowed to come into contact with the Pyrex glass of the reaction chamber a side reaction takes place, which in a superficial examination might be confused with a high temperature hydrolysis. The results of this study give no evidence for the existence of any appreciable reaction between a pure alkali halide (lithium bromide) and water vapor. Thermochemical computations show that the extent of the reaction should be very small, and would not be detectable within the experimental error of the method of analysis. It was found that an increase in temperature should favor the hydrolysis reaction. The results of the thermochemical computations are in agreement with the data obtained in this study.

ADVISER'S APPROVAL



I INTRODUCTION

Munger^{6*}, in his study of the high temperature reaction of potassium fluorides and potassium metaphosphate, found that there was an extensive loss of fluorine from the melts when such melts were held at high temperatures for extended periods of time. It was suggested that this loss of fluorine might be due to the high temperature hydrolysis of the melt.

The present study was undertaken to obtain some experimental data on the high temperature hydrolysis of alkali halides.

The possibility of the hydrolysis of molten halides at high temperatures has been suggested from time to time to explain the loss of halogen when such mixtures were heated for extended periods. For example, Eastman and Duschak² reported a ready reaction of lead chloride with moist air to yield HCl at low temperatures and Cl₂ at high temperatures. The loss of HCl from magnesium chloride hexahydrate when heated is well known.

More recently Hill and Andrieth³ have explained the loss of fluorine, which they observed when mixtures of equimolecular proportions of sodium fluoride and sodium metaphosphate are heated together, as being due to a high temperature hydrolysis of the mixture. This hypothesis they show to be consistent with the loss observed.

Finally Briner and Roth¹ have made an extensive study of the high temperature hydrolysis of alkali chlorides, with and without the admixture of such substances as kaolin and silica. These workers report considerable "hydrolysis."

* Please see bibliography for references.

II NATURE OF STUDY AND CONCLUSIONS

The experimental apparatus first designed and built followed the scheme employed by Briner and Roth¹.

This initial flow system allowed a gas, (air or nitrogen) saturated with water vapor to be passed through a heated tube containing the alkali halide (in a boat). The exit gases were collected in an absorption system to remove the acidic vapors. Chemical analysis was made on the material left in the boat as well as on the material collected in the absorption system.

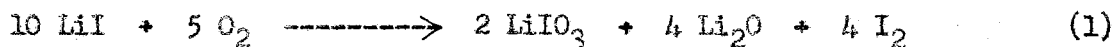
The final apparatus was a static system, wherein a sample of the alkali halide could be heated in contact with a given pressure of water vapor. The gaseous products were not collected, but the residue left in the boat was analyzed for halide.

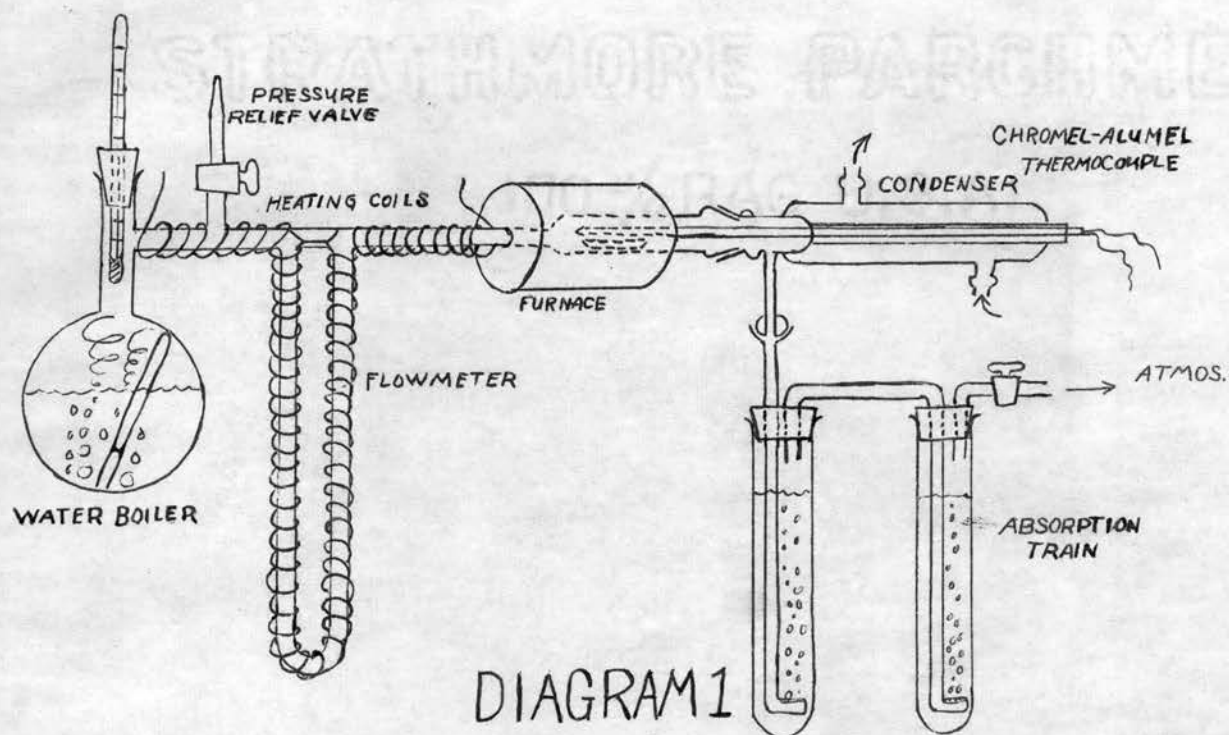
The results of these experiments give no evidence for the existence of any appreciable reaction between a pure alkali halide (lithium bromide) and water vapor. Various side reactions do occur which in a superficial examination might be confused with a high temperature hydrolysis.

III EXPERIMENTAL

Flow Systems. --- The original flow system in principle followed that described by Briner and Roth¹. It consisted of a boiler from which the generated water vapor passed through an electrically heated flow meter and delivery tube. This delivery tube was connected directly to the reaction chamber. The reaction chamber was surrounded by an electrically heated furnace the temperature of which was controlled by a "Brown Pyrovane Controller." A thermocouple of chromel-alumel was used to control the temperature of the furnace. A boat containing the salt was placed in the reaction tube and heated until the salt was melted before the water vapor was introduced. An absorption system, composed of a condenser and bubbling column was connected to the exit end of the reaction tube. This absorption train was designed to absorb any acidic gases produced by the reaction. An analysis was made on the residual material left in the boat as well as on the absorbed gases.

A sample of relative pure lithium iodide was selected for the first attempt at hydrolysis. The sample was placed in a ceramic boat (Firefrax) and inserted into the reaction tube. The furnace was then turned on to preheat the sample before exposing it to the water vapor. The flow system just described and represented in (Diagram 1) was used for this experiment. As soon as the temperature of the reaction tube became slightly warmer than 100°C. sublimation of the liberated iodine was shown by its characteristic dark violet vapor filling the reaction chamber and absorption train. Since air was not excluded from the system this reaction was to be expected as Simmons and Pickett¹⁰ have shown the following reaction to occur.





FLOW SYSTEM USING PURE WATER VAPOR

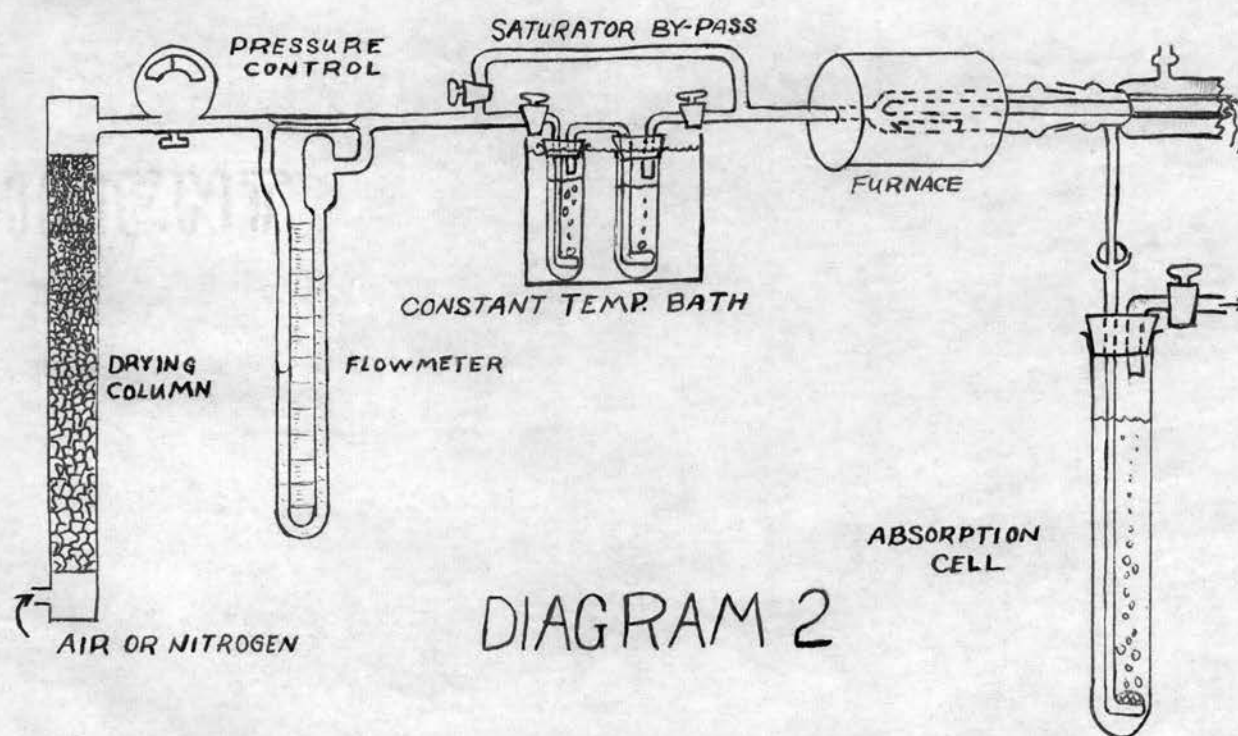


DIAGRAM 2

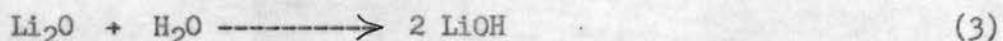
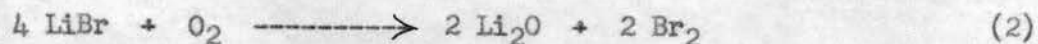
FLOW SYSTEM USING A CARRIER GAS

Because of the air oxidation of the lithium iodide and subsequent sublimation of the liberated iodine lithium bromide was selected as the salt to be used in the remainder of the experiments. Its melting point ($547^{\circ}\text{C}.$) is also below the softening point of Pyrex glass.

The method employing pure water vapor was used in the first attempt to hydrolyze lithium bromide. As long as only heated air was passed through the system it functioned perfectly, but upon the introduction of the water vapor the smooth flow of gas soon became intermittent. Condensation of the vapor in the cooler portions of the system leading to and from the reaction chamber was responsible for this condition. The pressure built up in the reaction chamber caused by the fact that the temperature of the reaction chamber was above the critical temperature of water ($347^{\circ}\text{C}.$) resulted in a back pressure which forced condensation in the cooler delivery tube. This condensed water was intermittently forced into the reaction chamber as a liquid. The interval of these "water charges" depended upon the frequency with which the delivery pressure exceeded the back pressure developed in the reaction tube. This method was therefore abandoned in favor of one which would give a smoother flow of water vapor and not be as susceptible to condensation in the various constricted and cooler portions of the delivery and exhaust tubes. (Diagram 2)

The system was modified so that the water boiler was replaced by an air supply, which had been previously run through a drying column to remove any foreign gases or solid particles. This air supply was connected to a flowmeter which led through a saturator surrounded by a constant temperature water bath held at $50^{\circ}\text{C}.$ From this saturator the "wet" air came into contact with the molten salt (LiBr) large quantities of bromine were released into the system. Analysis of the absorbed products showed

the presence of free bromine but no bromide. This is in keeping with the results found by Eastman and Duschak². A suggested mechanism for this reaction is:



For this reason the air was replaced with nitrogen as a carrier gas for the water vapor. This allowed the system to be swept free of oxygen before the water vapor was introduced. Only a minor modification of the apparatus was required to make this change. The system was so constructed that either "wet" or "dry" nitrogen could be allowed to flow through the system. When the system was flushed with "dry" nitrogen gas prior to and during the heating of the sample there was, for all practical purposes, no indication of any reaction. When the "wet" nitrogen was introduced there was no detectable change in the bromide content of the absorbed products, but there was a significant increase in the amount of free bromine produced. Since the nitrogen used was of a commercial grade it is possible that a small amount of oxygen present in the nitrogen was responsible for the first step of the suggested mechanism with the water vapor introduced completing the reaction.

After the reaction had been completed and the apparatus disassembled it was noticed that a considerable portion of the salt had either crawled or spattered from the boat. At this temperature the salt apparently reacted with the Pyrex glass of the reaction chamber. A platinum boat was therefore constructed to minimize this unfavorable side reaction. At this stage in the study it was believed that only the oxygen present in the nitrogen gas was responsible for the "pseudo hydrolysis."

A careful determination of the amount of water vapor delivered by the saturated nitrogen revealed that although the nitrogen was saturated when it left the saturator this amount of water vapor was not delivered into the reaction chamber. This again was caused by condensation in the delivery tube. The application of heat by electrically heated nichrome coils and the radiation of a heat lamp failed to keep the delivery of the water vapor at a constant rate.

Analysis of the products collected by the somewhat cumbersome absorption train indicated that the magnitude of the reaction was so small that the products were lost in the method of analysis. Only a trace of bromide could be detected in the absorbed products.

With the idea of building a system which would be free from condensation difficulties and give a more accurate method of analysis a static system was designed and constructed.

Static Systems. --- This system consisted of a reaction tube sealed at one end, and fitted with a ground glass standard taper joint large enough to allow the introduction of the platinum boat containing the salt, at the other. The rest of the system was connected to the reaction tube by a standard taper joint. To this connecting Pyrex tube was sealed a bulb which could be evacuated and used to draw off the gases resulting from the reaction. Another bulb was sealed into the system which served to meter in the water vapor. A third bulb was also attached so that a measured amount of air could be introduced into the system if desired. A closed end manometer was also connected to the system for the measurement of the change in pressure during the reaction as well as for the control of reproducible conditions (Diagram 3).

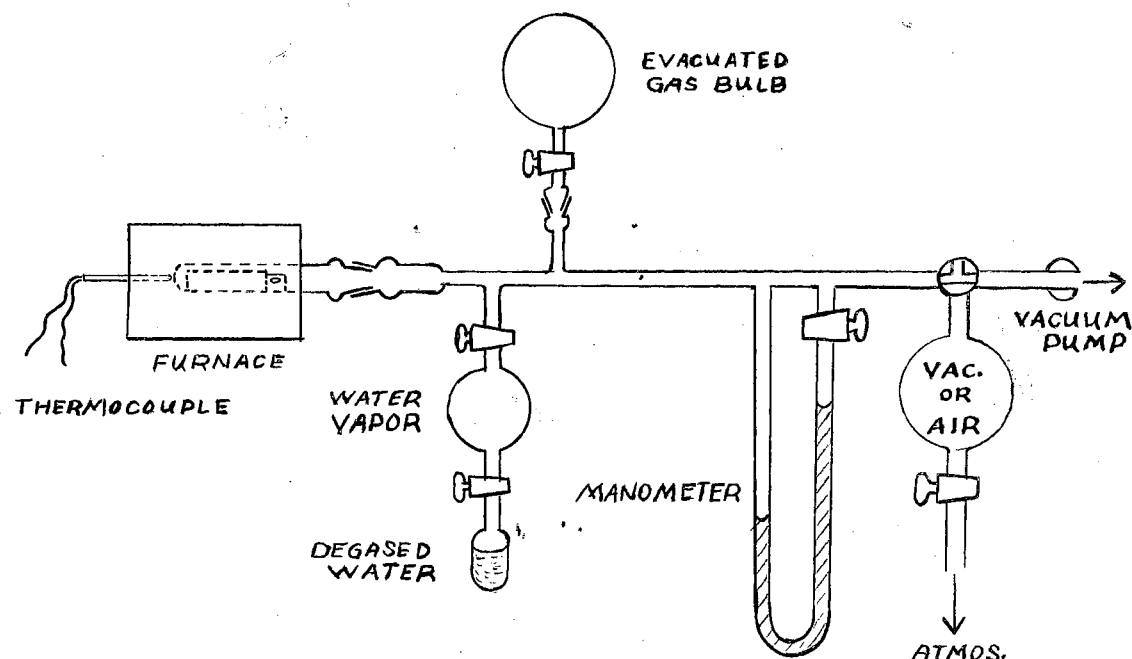


DIAGRAM 3

STATIC SYSTEM REDUCED PRESSURE

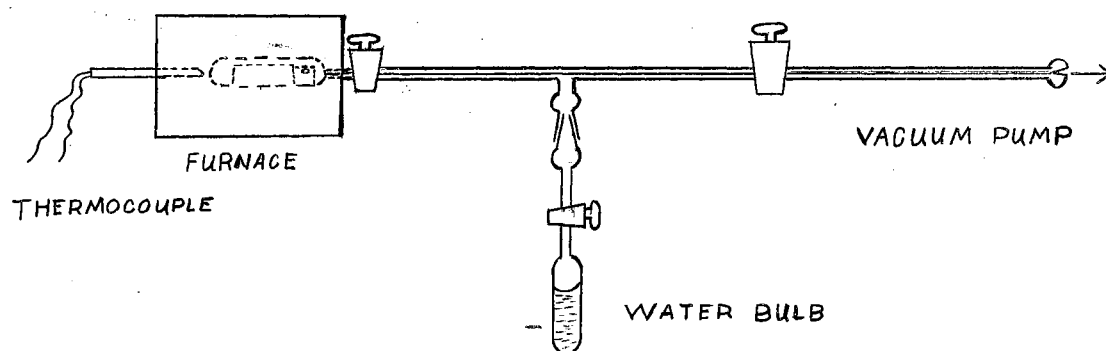


DIAGRAM 4

STATIC SYSTEM INCREASED PRESSURE

When in operation the sample was placed in the platinum boat and inserted into the reaction chamber, which in turn was placed in the furnace and then connected to the rest of the system by a ground glass joint. The entire system was evacuated to a pressure of about 6 mm., then the stopcock connecting the exhaust gas bulb to the system was closed and the furnace was turned on. While the furnace was attaining the reacting temperature, which was 547°C . or the melting point of LiBr , the vacuum pump was permitted to pump on the system. This was done so that any water of hydration or moisture adsorbed on any portion of the system would be pumped out of the system thereby not allowing any reaction to take place while the salt was being heated. When the reaction tube reached the desired temperature the vacuum pump was sealed off, by means of a stopcock, and a measured amount of water vapor was allowed to enter the reaction chamber. The manometer registered the rate at which the pressure in the system changed. Upon completion of the time of the reaction the evacuated bulb was opened to the system and this withdrew approximately 80% of the gases produced by the reaction. The furnace was turned off and the vacuum pump once again was allowed to pump out the remainder of the gases in the system while the furnace and reaction tube were cooling.

When the water vapor was first introduced the manometer indicated the pressure of the vapor present and thus knowing the volume of the system the amount of water vapor introduced could be calculated. Soon after the introduction of the water vapor the manometer showed that the vapor was being used up. This at first seemed a measure of the hydrolysis, but the analysis of the residual product showed the loss of bromide to be much too small to account for the reaction as indicated by the manometer. It

was found that there was still a small amount of reaction between the Pyrex glass of the reaction tube and the fumes from the molten salt. This reaction was indicated by an etched appearance to that portion of the reaction tube which was in the immediate vicinity of the platinum boat. This scale which was deposited on the walls of the reaction tube was insoluble in hot or cold, concentrated or dilute HCl, HNO_3 , Aqua Regia, and cold 6N NaOH. Boiling the reaction tube in a water bath while it was filled with 6N NaOH removed this scale, however this treatment also etched the glass. It was this reaction with the glass which was then believed to be responsible for the apparent hydrolysis.

An attempt to stop this etching action was initiated by making a graphite tube fitted with a graphite cap, which contained a small hole to allow the water vapor to come into contact with the molten salt. This graphite tube did keep the fumes from the molten salt from etching the glass and prevented any spattering of the salt on to the reaction tube.

Several attempts at hydrolysis were then made using the graphite tube. While this stopped the etching action on the Pyrex glass it also stopped the indication of any other reaction. Since the manometer showed no indication of any reaction it was removed from the system in an effort to cut down on the surface area of the glass tubing which would offer any chance for adsorption of the water vapor or the gases produced.

Removal and analysis of the gaseous products showed that there was very little if any reaction. This substantiated the results found when the analysis of the residue showed that there had been no loss of bromide from the reactants and therefore no hydrolysis.

Several methods were attempted to force more water vapor into the reaction chamber. One method was to allow the vapor pressure of the

water in the water bulb to come to equilibrium with the pressure in the system. This was done by simply making a direct connection from the water bulb to the system and surrounding the water bulb by a Dewar flask filled with water and held at a constant temperature (about 20°C.). This arrangement kept a constant pressure of water vapor on the reacting salt throughout the entire experiment. This treatment also failed to produce any reaction between the molten salt and the water vapor.

Another method was attempted to force the hydrolysis by forcing the water vapor into the reaction chamber under a higher pressure. This was done by surrounding the water bulb with a boiling water bath. Due to the evacuation of the system the water in the bulb boiled at a temperature below 100°C. and thus, the pressure of the vapor was not atmospheric pressure. No attempt was made to determine the exact pressures attained since, this treatment had no apparent effect on the reaction.

Still another method was tried in which increased pressures could be developed to the point of exploding the Pyrex glass reacting vessel (Diagram 4). This system consisted of a thick-walled Pyrex glass tube, containing the graphite tube, closed at one end and sealed to a thick-walled capillary tube at the other. This type of construction was employed to cut down on the amount of surface exposed and to permit maximum strength. Connected to the lead-off tube from the reaction chamber, by means of ground glass joint, was a small bulb filled with water. This arrangement enabled the water bulb to be removed and weighed on an analytical balance and thereby determine the amount of water and thus, the pressure developed within the system could be calculated. Connection was also made to a vacuum pump so that the system could be evacuated of

air or any foreign gases. The water was introduced by pumping the system down and then immersing the closed end of the reaction tube in a dry ice and ethyl acetate bath. When the end of the reaction chamber was cooled sufficiently the water vapor from the water bulb was allowed to enter the tube connected to the reaction chamber. This water vapor condensed and froze in the cooled end of this reaction chamber. With a little experimenting the time the water bulb was allowed to remain connected to the reaction chamber, for the introduction of the desired amount of water vapor into the system, was determined. The reaction tube, containing the sample, graphite tube, and the water vapor was then sealed off by a heavy-duty stopcock with a minimum of capillary tubing extending beyond the furnace. After the reaction time had elapsed the resulting gases were allowed to escape and the system evacuated and cooled.

With the above mentioned arrangement pressures as high as 12 atmospheres (calculated) were developed. Analysis of the products of the reaction after this treatment failed to show any indication of hydrolysis taking place. For example: One run showed that the bromide content of the residue in the graphite tube actually increased 0.14% while an identical run showed a loss of 0.36% of bromide put into the reaction vessel.

Preparation of Sample.---- The best grade of LiBr available was used in preparing the samples for this study. (Merck, N.F. 85-90% anhydrous, purchased 2-1-46) A small amount of this LiBr was placed in a clean dry platinum crucible and gently heated until all of the water of hydration and absorbed moisture had been driven off. The crucible and sample material was then heated to a somewhat higher temperature until the salt melted producing a viscous colorless liquid. The salt was kept in the molten state for approximately five minutes, and then it was poured

from the crucible on to a cleaned and polished stainless steel plate. When the melt had partially solidified it was broken into pieces small enough to be easily inserted into the graphite tube. These pieces were placed in a previously cleaned and dried weighing bottle, which was then placed in a desiccator to cool. This weighing bottle containing the fused LiBr was stored in the desiccator and removed only when weighing and removal of the sample required it. The LiBr removed from the weighing bottle was placed directly into the graphite tube, capped, inserted into the reaction chamber, and pumped free of moisture and air as quickly as possible. Since the LiBr is so very hygroscopic the less time it remained in contact with the moist atmosphere the more accurate was the weight of the sample taken.

Analytical Procedure. --- After the reaction was completed and the gaseous products removed the reaction chamber was allowed to cool. The graphite tube containing the sample was removed and placed in a desiccator to cool to room temperature. When the tube and sample reached room temperature they were removed from the desiccator and weighed. A sample of the residue from the tube was washed from the graphite tube into a 100 ml. volumetric flask with distilled water. The tube was then leached with more water and this added to the volumetric flask. The graphite tube and cap was then heated in the furnace, under vacuum, to the temperature of the original reaction and then cooled as before. Any residue which remained in the drying tube was washed into the volumetric flask. When the graphite tube and cap had again cooled to room temperature it was weighed again and the difference between the two weighings was taken as the weight of the sample titrated. The volumetric flask



Figure 1. Low Pressure Static System

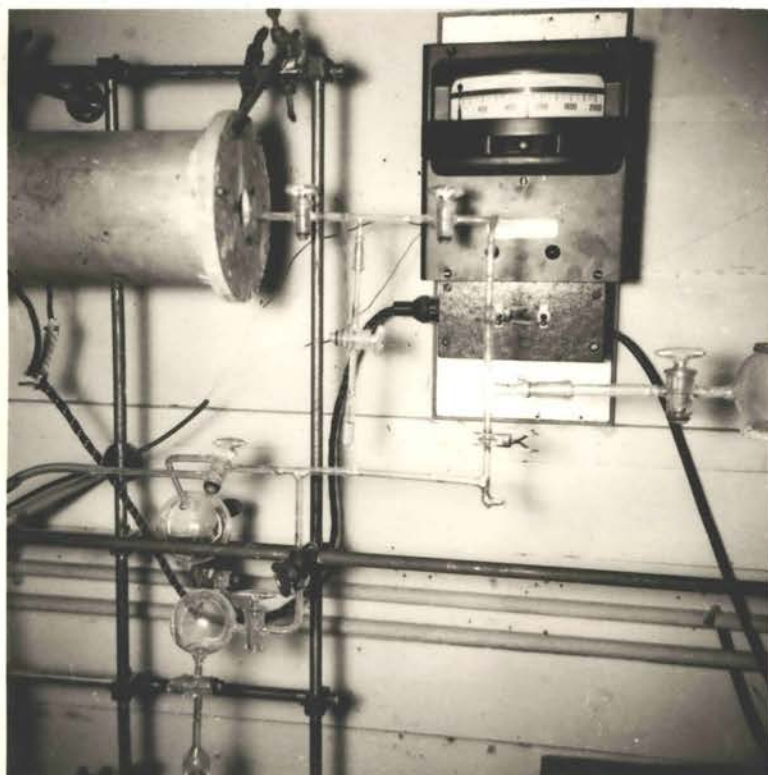


Figure 2. High Pressure Static System

was then filled with distilled water up to the mark and shaken thoroughly. Five ml. of the resulting solution was pipetted into each of three 50 ml. beakers. To each of these beakers was added one drop of Eosin-B indicator and six drops of dilute acetic acid. These samples were then titrated rapidly with a fresh solution of standardized AgNO_3 0.1000N using a micro-burett calibrated to one-fiftieth of a milliliter. The end point of the titration is marked by a definite change in color of the suspended precipitate from white to red along with coagulation of the precipitate.⁸

IV EXPERIMENTAL

Hydrolysis of LiBr

Flow System

- (a) Pure water vapor -- no numerical data available
- (b) Air saturated with water vapor at 50°C. -- liberation of Br₂.
- (c) Nitrogen saturated with water vapor at 50°C.

Table I

Reaction time in minutes	Absorption train			Residue		
	Br ₂	Br ⁻	pH	Br ₂	Br ⁻	pH
33	much	trace	5	none	yes	5
60	yes	trace	4	none	yes	4
* 68	yes	trace	4	none	yes	4
94	yes	none	4	none	yes	4
* 24	none	none	5	none	yes	5
30	yes	trace	4	none	yes	5
49	much	none	5	none	yes	5
* 162	yes	trace	-	none	yes	-
101	none	none	5	none	yes	5
105	none	none	5	none	yes	5

* indicates runs in which water vapor was not introduced

Observations of the above data show that in no case was any free bromine present in the residual material in the boat. The pH of the absorbing solution remained practically unchanged. This would tend to indicate that very little reaction had taken place.

Hydrolysis of LiBr

Static System

Table II

(a) Water vapor allowed to enter under a reduced pressure of 6 mm.

Reaction time in minutes	Weight of sample in grams	Weight of sample titrated	Weight of sample accounted for by titration	Milliliters of AgNO_3 0.1000 N	Percent change by reaction
105	2.4612	2.008 #	2.007	11.556	- 0.05
* 240	1.8292	1.493 #	1.510	3.694	+ 1.14
* 30	3.0426	3.043	3.017	17.370	- 0.36
30	3.9711	3.971	3.925	22.593	- 1.16
* 30	1.5388	1.539	1.534	8.768	- 0.26
30	1.0885	1.089	1.064	6.080	- 2.26
15	1.3997	1.400	1.393	8.020	- 0.50
30	1.1366	1.137	1.121	6.453	- 1.41

(b) Water vapor entered system under vapor pressure at 100°C.

30	1.7656	1.684 ##	1.688	9.716	+ 0.24
30	1.5894	1.566 ##	1.591	9.160	+ 1.60

(c) Water vapor in system calculated to be at pressures of 4 and 12 atmospheres respectively.

30	2.0478	2.020 ##	2.012	11.584	- 0.39
30	1.3869	1.346 ##	1.347	7.756	+ 0.07

* Indicates runs in which water vapor was not introduced.

Corrected for water content (approximately 18.4%).

Corrected for actual amount taken from graphite tube.

Sample Calculation

Weight of weighing bottle plus sample 33.6165 gms.
 Weight of weighing bottle 32.2296 gms.
 Weight of sample 1.3869 gms.

Weight of graphite tube and cap 13.7862 gms.
 Weight of sample 1.3869 gms.
 Total weight of graphite tube, cap and sample . 15.1731 gms.

Weight of tube, cap, sample after reaction. . . 15.1591 gms.
 Weight of tube and cap after removing sample. . 13.8136 gms.
 Weight of sample titrated 1.3455 gms.

Average ml. of 0.1 N AgNO_3 to titrate 1/20 of sample. . 7.756 ml.

Temperature of reaction = 547°C . Time of reaction = 30 min.

Internal volume of reaction chamber = 21.85 cubic cms.

$$\frac{0.1 \times 86.86 \times 20 \times 7.756}{1000} = 1.347 \text{ gms. of LiBr}$$

Weight of sample titrated = 1.346 gms.
 Weight accounted for = 1.347 gms.
 Excess of LiBr = 0.001 gms.

$$0.001 \div 1.346 = 0.00074 = \underline{0.07\%} \text{ increase in LiBr}$$

The internal volume of the reaction chamber was determined by weighing the reaction chamber and attached capillary tube; then measuring, by immersion, the external volume of the reaction chamber and tube. From its weight and density and also the density and weight of the graphite tube and cap the internal volume was calculated. Using this volume the required amount of water was allowed to enter which would give the desired pressures when the reactants were heated. In above experiment the pressure of 12 atmospheres (calculated) was developed.

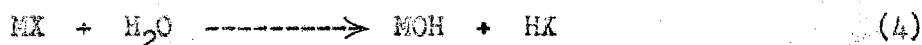
Discussion of Experimental Data. --- Although the data obtained from this study do not have the precision that is desirable in work of this nature, they do tell us some valuable information. This inconsistency is partly due to the fact that the technique of handling the sample as well as purification of the sample were improved as the study progressed. This was especially true of the method used to determine the amount of sample actually titrated. In the early part of the study it was not known that part of the sample was lost through absorption in the graphite of the tube. When this was realized the method of obtaining the sample described in the analytical procedure was adopted. The values obtained in the later part of the study are therefore more indicative of the true values. The hygroscopic nature of the salt remained the largest single error introduced into the analytical method. This error was minimized as much as possible by rapid handling when the salt was exposed to moist air.

An arithmetical average of the results of all the experiments is - 0.24%. The reliability of this figure determined by dividing the average deviation by the square root of the number of cases is $\pm 0.13\%$. This indicates that about 0.4% reaction is the maximum and 0.1% the minimum. If only the final four results are considered, since it is known that technique and accuracy were improved in these experiments, the result becomes + 0.38% $\pm 0.21\%$, or more bromide after the reaction than before. This, of course, is absurd and becomes meaningless as a numerical value. Since the average weight of the samples is 1.654 gms. this means an average increase of 6 mgs., which in view of the hygroscopic nature of the salt, is understandable. In brief this tells us that there is no evidence for any appreciable hydrolysis.

V THEORETICAL DISCUSSION

Calculation of the Equilibrium Constants for the Hydrolysis of Alkali Halides. --- The thermochemical data for the alkali halides and their related compounds are incomplete, with the exception of the data for the sodium compounds. All of the standard heats of formation required are known and the absolute entropies are known, except those of LiBr, LiI, and KOH. Using the data available it is possible to make a good estimation of the values of the absolute entropies for the compounds where the data are missing. Therefore the standard free energies and consequently the equilibrium constant for a temperature of 298°K. may be computed. The high temperature heat capacities of these compounds are not well known, therefore only in the case of the sodium compounds may an exact calculation of the equilibrium constants at high temperatures be made.

The computations for the thermodynamic equilibrium constant (K_a) for the hydrolysis of sodium chloride at 298°K. follows:



$$\Delta F^\circ_{298} = -RT \ln K_a \quad \text{and} \quad \Delta F^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$$

$$\text{therefore:} \quad -\log K_a = \frac{\Delta H^\circ_{298} - T\Delta S^\circ_{298}}{2.303 \times RT} \quad (5)$$

ΔH°_f KCal/mole @ 298°K. ⁷	S° cal./deg./mole @ 298°K. ⁴
NaOH - 101.99	NaOH 13.80
NaCl - 98.23	NaCl 17.30
HCl - 22.06	HCl 44.66
H ₂ O - 57.80	H ₂ O 45.13

$$\frac{\Delta H^\circ_{298}}{2.303 RT} = \frac{(-101.99 + (-22.06)) - (-98.23 + (-57.80))}{1.987 \times 2.303 \times 298.2} = + 23.50$$

$$\frac{\Delta S^\circ_{298}}{2.303 R} = \frac{(13.80 + 44.66) - (17.30 + 45.13)}{2.303 \times 1.987} = - 0.87$$

$$-\log K_a = + 23.50 - (-0.87) = + 24.37 \quad \text{thus, } K_a = 4.3 \times 10^{-25}$$

The Nernst Approximation equation for determining the equilibrium constant when the absolute entropies are not known follows:

$$\log K_p = \frac{-\Delta H}{2.303 RT} + 1.75 \Delta n \log T + \sum (nC) \quad (8)$$

Where: ΔH is the heat of reaction, Δn the difference between the number of moles of gaseous products and reactants, T the absolute temperature, and C the chemical constants for the gaseous substances involved in the reaction

In reaction (4) $\Delta n = 0$ and $\sum (nC) = C_{HX} - C_{H_2O}$; thus, for the reaction

of NaCl one obtains $C_{HCl} - C_{H_2O} = 3.0 - 3.6 = -0.6$

$$\begin{aligned} \text{and } \log K_p &= \frac{(-31980)}{4.567 \times 298} - 0.6 = -12.46 - 0.60 \\ K_p &= 7.9 \times 10^{-25} \end{aligned} \quad (9)$$

Table III Thermochemical Constants⁹

HCl = 3.0	HI = 3.4
HBr = 3.2	H ₂ O = 3.6

Since when dealing with numbers of this magnitude the mantissa is probably not significant. The two methods give results which agree very favorably. Using both methods and estimating the missing values for the absolute entropies of KOH, LiBr, and LiI the following equilibrium constants were computed.

Table IV

Equilibrium Constants for the Hydrolysis of Alkali Halides (298.16°K.)

	K_a	K_p (Nernst)	K_a/K_p (Nernst)
LiCl	1.5×10^{-13}	8.3×10^{-14}	1.8
* LiBr	3.9×10^{-13}	3.4×10^{-13}	1.1
* LiI	8.1×10^{-10}	8.5×10^{-10}	1.0
NaCl	4.3×10^{-25}	7.9×10^{-25}	0.5
NaBr	6.5×10^{-26}	1.8×10^{-25}	0.4
NaI	5.4×10^{-24}	2.3×10^{-23}	0.2
* KCl	6.2×10^{-30}	2.4×10^{-29}	0.3
* KBr	4.1×10^{-32}	2.5×10^{-31}	0.2
* KI	2.1×10^{-31}	1.8×10^{-30}	0.1

* Absolute entropies estimated for LiBr, LiI, and KOH

It is seen that the values obtained for the lithium and potassium salts by the two methods compare almost as well as do the values for the sodium salts where all the thermal data are available.

The calculation of the equilibrium constants at higher temperatures may be made using the equation:

$$\ln K = \int \frac{\Delta H}{R T^2} dT + I \quad (10)$$

To do the indicated integration requires knowledge of how the heat of the reaction varies with temperature. This in turn requires knowledge of the variation of the heat contents with temperature. Since the solid substances will melt as the temperature is raised, heats of fusion must also be known. Only in the case of the sodium compounds may all of these factors be considered in the calculation. Thus, it is possible to make only approximate calculations for the lithium and potassium compounds.

If one assumes that ΔH does not vary with temperature then one may write equation (10) as:

$$\ln K = - \frac{\Delta H}{R T} + I \quad (11)$$

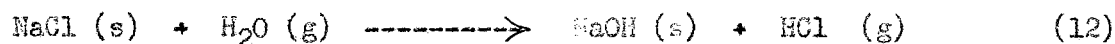
Using this equation (11), the equilibrium constants for the reactions have been calculated for a temperature of 820°K. (The temperature of this experimental work.) The results of these computations are tabulated in Table V.

Table V

Equilibrium Constants for the Hydrolysis of Alkali Halides (820°K.)

	Cl	Br	I
Li	1.25×10^{-5}	1.8×10^{-5}	2.7×10^{-4}
Na	3.5×10^{-10}	2.0×10^{-10}	9.6×10^{-10}
K	3.8×10^{-12}	6.0×10^{-13}	1.2×10^{-12}

An estimate of the error introduced by the assumptions that ΔH is constant may be made by considering the following calculation of the variation of the heat of reaction with temperature.



$$\Delta H = \Delta H_{298}^{\circ} + \int_{298.16}^T \Delta C_p dT \quad (13)$$

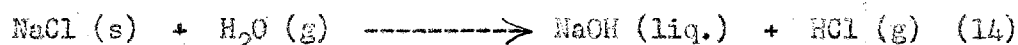
$$\Delta H_{595} = 31,983 + \int_{298.16}^{595} \Delta C_p dT \quad (13')$$

Computing ΔC_p from the data given by Kelly⁵, then substituting in equation (13') and integrating one obtains:

$$\Delta H_{595} = 31,983 + \left[7.39(595.0 - 298.2) - \frac{5.36 \times 10^{-3}}{2} \left((595)^2 - (298.2)^2 \right) \right]$$

$$\Delta H_{595} = 31,983 + 2,193 - 711 = 33,465 \text{ cal.}$$

Since $\Delta H_{\text{(fusion)}}$ for NaOH is 2,000 cal. the heat of the reaction



becomes: $\Delta H_{595} = 33,465 + 2,000 = 35,465 \text{ cal.}$

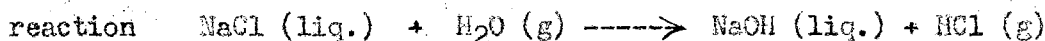
The heat of the reaction (14) is then calculated at 1073°K. (m.p. NaCl) using the same procedure used for equation (12).

$$\Delta H_{1073} = 35,465 + \int_{595}^{1073} \Delta C_p dT$$

$$\Delta H_{1073} = 35,465 + \left[8.19(1073 - 595) - \frac{5.36 \times 10^{-3}}{2} \left((1073)^2 - (595)^2 \right) \right]$$

$$\Delta H_{1073} = 35,465 + 3915 - 2136 = 37,244 \text{ cal}$$

The heat of fusion of NaCl is 6,850 cal. therefore, the heat of the



is $\Delta H_{1073} = 37,244 - 6,850 = 30,394 \text{ cal.}$

It is apparent that the variation of ΔH with temperature is small and that the over all effect of the heat of fusion of the salts is also small.

Discussion of the Extent of Reaction Expected. --- The thermodynamic equilibrium constant for the hydrolysis reaction (equation 4) is:

$$K = \frac{a_{\text{MOH}} \cdot a_{\text{HX}}}{a_{\text{HX}} \cdot a_{\text{H}_2\text{O}}}$$

If the two liquid salts are completely miscible and are considered to form an ideal solution, then the activity of the hydroxide is equal to its mole fraction N_{MOH} and since the extent of reaction is small the activity of the alkali halide is approximately unity. The activity of the gases are approximately equal to partial pressures. Then equation (15) becomes:

$$\frac{N_{\text{MOH}} \cdot P_{\text{HX}}}{P_{\text{H}_2\text{O}}} = K \quad (16)$$

The limit of error in the experimental work of this study is likely less than 0.5% (on the analysis). Hence, assuming a sample weight of 1.5 gm. the mole fraction of LiOH in the melt could not be greater than about 5×10^{-3} . In the last high pressure static experiment a calculated pressure of 12 atmospheres of water vapor was used. Therefore, the partial pressure of the HBr in the gas phase would be approximately:

$$P_{\text{HBr}} = \frac{1.8 \times 10^{-5} \times 12}{5.0 \times 10^{-3} \times 760} = 5.7 \times 10^{-5} \text{ (mm.)}$$

Influence of Acidic Oxides on the Extent of Reaction. --- Briner and Roth¹ have explained their appreciable yields of HCl from the reaction of water on mixtures of alkali chlorides and silica, alumina, and kaolin by the thermodynamically spontaneous reaction which occurs between alkali oxides and such acid oxides. They have made approximate thermochemical calculations which they suggest are indicative that the above explanation is correct. For the reaction $2 \text{NaCl} + \text{H}_2\text{O} + \text{SiO}_2 \longrightarrow \text{Na}_2\text{SiO}_3 + 2 \text{HCl}$ (17)

they compute a ΔF° of 40,800 cal. at 298°K. and 19,860 cal. at 1073°K. These calculations were repeated and essentially the same results were obtained. In view of the smallness of the equilibrium constant it seems dubious that this explanation is adequate, although for their flow system it may be sufficient to explain the yields. However, the yields obtained appear inconsistent with these calculations.

VI CONCLUSIONS

From the results of this study it was found that all oxygen must be excluded from the system if any attempt to measure the hydrolysis is to be made. Since Briner and Roth¹ make no mention of removing oxygen from the system, it is possible that a part of the large extent of "hydrolysis" that they reported was due not to hydrolysis but rather oxidation of the salt. This is analogous to the reaction reported by Simmons and Pickett¹⁰.

It was also found that the Pyrex glass of the reaction tube would react with the molten salt and give the effect of a high temperature hydrolysis. Briner and Roth¹ report that they carried out their reactions in a glass reaction chamber with the salt contained in a platinum boat. It was found in this study that the salt did not remain in the platinum boat, but either crawled or spattered on to the reaction chamber giving rise to a side reaction which does produce an acid. This could easily mislead one to the conclusion that hydrolysis was taking place.

The effect of time, pressure of the water vapor, and temperature of the reaction did not have any detectable effect on the extent of the hydrolysis.

It was found that under pressures higher than atmospheric the salt was very strongly absorbed in and adsorbed on the graphite reaction tube.

From the results of this study there are no indications of a high temperature hydrolysis of lithium bromide. Thermodynamic calculations are in agreement with this experimental conclusion.

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BIOGRAPHY

Robert Torolf Johansen was born in Minneapolis, Minnesota on June 13, 1924. His family moved to Wishek, North Dakota when he was six months of age. In June of 1930 he moved to Bismarck, North Dakota where he received his primary education in the public schools. In September of 1938 he again moved to Wishek where he lived until June of 1940 at which time he moved to Enderlin, North Dakota. There he completed his high school work and graduated from the Enderlin High School in May 1942.

He worked for the Lockheed Aircraft Corporation of Glendale, California for one year prior to his enlistment in the United States Army Air Force. He entered the Army Air Force as an aviation cadet in July, 1943. He graduated as a Navigator from the Selmon Field, Advanced Navigation School, Monroe, Louisiana in December, 1944 and received a commission as second lieutenant in the Army of the United States.

On September 9, 1945 he married Norma Jean Smith of Blanchard, Oklahoma.

In November, 1945 he was ordered to peace-time inactive duty. After leaving the service he enrolled as a student at Jamestown College, Jamestown, North Dakota. He was awarded the degree of Bachelor of Science in June, 1948.

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