[Contribution from the Department of Chemistry, St. Louis University]

A Study of Some Reactions between Dry Inorganic Salts

By E. B. Thomas and Lyman J. Wood

In a report made by the senior author at the Denver Meeting on certain salt mixtures it was shown that potassium chloride and sodium bromide interact with each other when the salts are fused, the reaction going practically to completion. This reaction has been studied in detail both below and above the fusion point. Several other reactions have also been investigated by means of the x-ray spectrograph and are reported below.

Methods and Apparatus

Each mixture examined was weighed out carefully, mixed thoroughly and heated in an electric furnace. Fused mixtures were kept above the fusion temperature for a few minutes, after which time they were taken from the furnace and poured onto a brass plate previously cooled in ice water. Immediately after pouring the molten mixture was stamped from above with another cold plate. The result was almost instantaneous crystallization.

The apparatus used for x-ray examinations was the General Electric Multiple Diffraction Spectrograph. The powder method was used for all tests. The powdered sample was passed through a 200 mesh screen and sealed in a thin-walled glass tube having a maximum outside diameter of 0.9 mm. The powder was exposed to the Mo α doublet for 500 to 600 m. a. hours, the x-rays being filtered through zirconia to make them nearly monochromatic. The film radius was 20.3 cm. The unavoidable error is believed to be about plus or minus 0.006 Å. for a cube edge of 5 to 6 Å., which is about the accuracy reported by Davey[1] using a similar laboratory procedure.

All film measurements were made by direct comparisons with standard sodium chloride lines on the opposite edge of the film, the NaCl 400, 331 and 420 interference lines being used for this purpose. For accurate measurements of cube edges, lines corresponding to interplanar distances in the range of 1.3 to 1.6 Å. (in the same range as the standard sodium chloride lines) were selected. The authors believe that this method of determining the cube edge has an important advantage over the use of all lines on the film as has frequently been done. In the first place it is obvious that interference lines corresponding to interplanar distances greater than 2 Å. should not be used since the unavoidable error in measuring is approximately ten times as large as in the range selected. In the second place lines too far out from the zero are not convenient since any error made is multiplied by a very large factor in calculating the cube edge and also excessive time of exposure is required to ensure lines heavy enough to measure accurately.

Mack, Havighurst and Blake[2] have shown that greater accuracy is obtained by calibrating each section of the film, *i. e.*, by selecting calibrating lines in the same range as the unknown lines. The method described above has been shown to produce accurate and reproducible results, as can be seen by referring to the data given below. It goes without saying that all the lines (frequently as many as 18 or 20) were measured in order to determine the pattern or patterns present, all lines being accounted for in the manner shown in Table II although space does not permit publishing all in detail. The Wyckoff method of mixing the standard with the unknown could not be used if sodium chloride was to be the standard since many of the mixtures contained sodium chloride. In order to determine the amount of error introduced due to the difference in densities of sodium chloride and an unknown when the two are photographed on opposite edges of the film, a trial run was made with pure potassium bromide as unknown and pure sodium chloride as standard. A cube edge value of 6.567 Å. was obtained for potassium bromide compared with 6.570 Å., the preferred value reported in the "International Critical Tables." In some cases flour was mixed with the heavier samples in order to minimize the effect of the difference in densities and also to cut down the time of exposure.

Experimental Results

In order to study in more detail the reaction $KCl + NaBr \longrightarrow KBr + NaCl$ mentioned above, a series of binary mixtures of KCl-KBr, KCl-

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(1) Davey, *Phys. Rev.*, **2**, 143 (1923).

(2) Mack, Havighurst and Blake, This Journal, **46**, 2368 (1924).

NaCl, NaCl–NaBr and NaCl–KBr of various compositions were made up and examined with the x-ray spectrograph. All of these salts crystallize in the sodium chloride type of lattice and the cube edges range from 5.628 Å. for NaCl to 6.570 Å. for KBr. The chemicals used were of C. P. quality for all mixtures. The results obtained are shown in Table I.

TABLE I

RESULTS OF X-RAY ANALYSIS OF BINARY MIXTURES

Mixture number	Composition in mole %	Phase I Indices *h k l*	Phase I *d* in Å.	Phase I Cube edge = *a*	Phase I Remarks	Phase II Indices *h k l*	Phase II *d* in Å.	Phase II Cube edge = *a*	Phase II Remarks
19a	NaCl 50	400[a]	...	...	For pure NaCl	400	1.571	6.284	For pure KCl
	KCl 50	420	1.257	5.628	$a = 5.628$	420[a]	...	...	$a = 6.280$
		422	1.149	5.628	No KCl diss.	422	1.282	6.280	No NaCl diss.
42	KBr 85	400	1.634	6.536	For a solid soln. of this				No lines for a second
	KCl 15	420	1.461	6.534	compn.				phase obs.
		422	1.333	6.530	$a = 6.526$				
2W	KBr 50	400	1.607	6.428	For a solid soln. of this				No lines for a second
	KCl 50	420	1.436	6.426	compn.				phase obs.
		422	1.309	6.416	$a = 6.425$				
43	NaBr 50	400	1.452	5.808	For a solid soln. of this				NaCl lines detected (faint)
	NaCl 50	420	1.300	5.814	compn.				
		422	1.186	5.810	$a = 5.784$				
1Y	NaCl 85	400	1.421	5.684	For a solid soln. of this				No lines for a second phase
	NaBr 15	331	1.302	5.676	compn.				obs.
		420	1.271	5.684	$a = 5.674$				
44	NaCl 50	400[a]	...	...	NaCl appears to be sl. sol.	222[a]	...	...	For pure NaCl
	KBr 50	420	1.464	6.548	in KBr. ($a = 6.570$)	420	1.260	5.634	$a = 5.628$
		422	1.338	6.554		...	...	...	

[a] Double line, *i. e.*, a line from each pattern occurred at about this position and hence neither could be measured accurately.

Vegard[3] investigated the system KCl–KBr and found it completely miscible in all proportions in the solid state. Vegard's results have since been confirmed by other workers[4] and in the present work (Mix No. 42 and No. 2W, Table I). From his work with KCl–KBr mixtures Vegard was able to state the "Additivity Law." Although it is by no means certain that the "Additivity Law" holds for all substitutional solid solutions, it does seem to hold very well for the type of solid solution dealt with in this paper. One of the purposes of the present work has been to see how well x-ray measurements from this type of salt mixture can be explained in terms of the "Additivity Law." Its validity has therefore been assumed.

It was already known that sodium chloride and potassium chloride are at most only a very little soluble in each other in the solid state at room temperature. G. Tammann[5] reported a continuous series of mixed crystals between 500 and 660°. R. Nacken[6] found that for a mixture of 65 mole per cent. of sodium chloride and 35 mole per cent. of potassium chloride the solid solution which exists at higher temperatures unmixes at slightly under 500° and that pure sodium chloride exists just under 300° and pure potassium chloride somewhat below 250°.

Havighurst, Mack and Blake[4a] using x-ray diffraction methods, report that about 2% of sodium chloride dissolves in potassium chloride and a few per cent. of potassium chloride in sodium chloride at room temperature. These conclusions were based upon two measurements which appear to be wholly inconsistent with each other. In this work it was found possible to check one of these two measurements to within 0.001 Å. (Mix No. 19a, Table I), from which results it is concluded that sodium chloride and potassium chloride are almost if not completely insoluble in each other in the solid state at room temperature.

Sodium bromide is reported to form a solid solution with sodium chloride up to 35% sodium bromide.[4a] Results are shown in Table I for a 50 mole per cent. mixture of sodium bromide and sodium chloride (No. 43). It is to be observed that the cube edge for the solid solution was larger than the calculated value, the observed

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(3) Vegard, *Z. physik*, **5**, 16 (1921).

(4) (a) Havighurst, Mack and Blake, THIS JOURNAL, **47**, 29 (1925); (b) Barone, *Atti Accad. Lincei*, **14**, 215–217 (1931).

(5) Tammann, *Nachr. Ges. Wiss. Göttingen*, 422–427 (1919).

(6) Nacken, *Tübingen Sitzb. kgl. preuss. Akad.*, 192–206 (1918).

value being 5.811 Å. and the calculated 5.784 Å. Another 50–50 mixture made up in a similar manner showed a cube edge of 5.834 Å. The direct interpretation of these results would be that the solubility of sodium chloride in sodium bromide has been exceeded and that there should be some pure sodium chloride in the mixture. After carefully clearing the film somewhat with cyanide some very faint lines corresponding to part of the sodium chloride pattern were found. The spectrograms of the annealed mixture revealed these lines more clearly. These results with those mentioned above indicate that sodium chloride and sodium bromide are not completely miscible, and that their miscibility depends upon the heat treatment which would account for the two somewhat different results reported above.

The detailed results obtained for duplicate runs for a KCl–NaBr mixture with an 80–20 mole per cent. composition are shown in Table II. It is clear from the table that the observed values for d from the duplicate runs agree with each other very closely. All of the lines are accurately accounted for on the basis of two face-centered patterns. The lines for one pattern correspond closely to lines for pure sodium chloride. Lines of the other pattern are very close to the positions expected for a solid solution of potassium chloride and potassium bromide although no potassium bromide was put into the mixture. The obvious explanation is that potassium chloride and sodium bromide have reacted according to the equation $8KCl + 2NaBr \longrightarrow 2KBr + 2NaCl + 6KCl$ and that the resulting potassium bromide has formed a solid solution with the residual potassium chloride. It is very interesting to note that the reaction appears to go to completion. As early as 1903 Ruff and Plato[7] reported a eutectic mixture of potassium bromide and sodium chloride having the composition of 54 mole per cent. potassium bromide. Brönsted and Petersen[8] arranged a cell in which this reaction could go in aqueous solution. The e. m. f. was found to be +0.0531 volt from which the equilibrium constant has been calculated to be $K = 12$ (approx.).

In order to study the reaction further a KBr–NaCl–KCl mixture having the composition 20–20–60 mole per cent. (see reaction above) was made up, and photographed on one edge of a film with the 80–20 mixture of potassium chloride and potassium bromide on the other edge. The film obtained showed identical patterns on its two edges, indicating clearly that potassium chloride and sodium bromide reacted with each other as indicated above.

TABLE II

MIXTURE 41, KCl 80 MOLE PER CENT., NaBr 20 MOLE PER CENT. STANDARD OF COMPARISON, NaCl

	Film L-31		Film L-22						
Line Number	Intensity	d(obs.)	Intensity	d(obs.)	Indices hkl	d Calcd. for $d_{200} = 3.173$	d Calcd. for a 75–25 KCl-KBr solid soln.^{c}	Indices hkl	d Calcd for NaCl
1	10	3.17	10	3.165	200	3.173	3.176		
2	4	2.80	2	2.81				200	2.814
3	9	2.24	9	2.24	220	2.244	2.246		
4	2	1.988	1	1.989				220	1.990
5	4	1.829	4	1.829	222	1.832	1.833		
6	^{a}	1.627	..	...				222	1.624
7	2	1.585	2	1.584	400	1.587^b	1.588		
8	4	1.419	7	1.418	420	1.419^b	1.420	400	1.407
9	3	1.296	5	1.293	422	1.295^b	1.297		
10	0.5	1.260	^{a}	1.259				420	1.259
11	.5	1.148	^{a}	1.150				422	1.149
12	1	1.120	0.5	1.121	440	1.122	1.123		
13	2	1.058	1	1.058	442 600	1.058	1.059		
14	1	1.002	0.5	1.002	620	1.003	1.004		
15	1	0.957			622	0.958	0.957		
16	^{a}	.939						442 600	0.938
17	^{a}	.917			444	.916	.917		
18	^{a}	.882			640	.880	.881		
19	0.5	.850			642	.848	.849		
20	^{a}	.771			820 644	.770	.770		

^{a} Very faint. ^{b} d_{200} Calcd. from d_{400}, d_{420}, d_{422}. ^{c} Calculated on the assumption of complete conversion of NaBr to KBr.

Table III shows the results obtained from a series of KCl–NaBr reactions with an excess of sodium chloride and potassium bromide as shown in the table. It has been pointed out above (Table I) that potassium bromide and potassium chloride form a solid solution with each other in all proportions and that sodium bromide and sodium chloride form a solid solution with each other within limits. It seems clear from the results for numbers 32a, 38 and 40 that potassium bromide present in the original mixture or formed by the reaction forms a solid solution with any excess potassium chloride and that sodium chloride is left as the pure salt. In the case of mixture 33, sodium bromide is present in excess instead of potassium chloride and a solid solution of sodium chloride and sodium bromide results, the potassium bromide being left as a pure component. The value obtained for the cube edge of potassium bromide in this case is slightly

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(7) Ruff and Plato, *Ber.*, **36**, 2357 (1903).

(8) Brönsted and Petersen, *Det. Kgl. Danske Videnskab. Selskab Math. fys. Medd.*, **1**, No. 3 (1917).

TABLE III

SHOWING X-RAY DATA FOR A SERIES OF REACTIONS BETWEEN KCl AND NaBr WITH EXCESS NaCl AND KBr AS SHOWN IN THE EQUATIONS

Mixture number	Composition before fusion	Assumed composition after fusion
32a	$30KCl + 20NaBr + 20KBr + 30NaCl \longrightarrow$	$40KBr + 10KCl + 50NaCl$
	KBr-KCl phase $a = 6.525_{\text{Obs. I}}, 6.521_{\text{Obs. II}}, 6.512_{\text{Calcd.}}$;	NaCl phase $a = 5.634^{a}$
38	$40KCl + 20NaBr + 40NaCl \longrightarrow$	$20KBr + 20KCl + 60NaCl$
	KBr-KCl phase $a = 6.438_{\text{Obs. I}}, 6.439_{\text{Obs. II}}, 6.426_{\text{Calcd.}}$;	NaCl phase $a = 5.630$
40	$24KCl + 20NaBr + 56NaCl \longrightarrow$	$20KBr + 4KCl + 76NaCl$
	KBr-KCl phase $a = 6.524_{\text{Obs. I}}, 6.521_{\text{Obs. II}}, 6.522_{\text{Calcd.}}$;	NaCl phase $a = 5.634$
33	$30KCl + 40NaBr + 30NaCl \longrightarrow$	$60NaCl + 10NaBr + 30KBr$
	NaCl-NaBr phase $a = 5.663_{\text{Obs.}}, 5.673_{\text{Calcd.}}$;	a for pure KBr $= 6.57, 6.558_{\text{Obs.}}$

[a] Accepted cube edge for pure NaCl is 5.628.

less than the accepted value but corresponds almost exactly with the value obtained when a 50-50 mixture of potassium bromide and sodium chloride (No. 44, Table I) was fused. It seems possible that a small amount of sodium chloride is dissolved in the potassium chloride.

Table IV shows the results obtained from a 50-50 mixture of potassium chloride and sodium bromide which was ground together vigorously in a large mortar for fifteen minutes but which was not heated in the furnace. It is clear that some reaction to form potassium bromide and sodium chloride has occurred and that neither KCl–KBr nor NaCl–NaBr solid solutions have been formed and furthermore that the reaction has not gone to completion since all four patterns are present. Judging from the intensities of the lines it might be estimated that about half of the KCl–NaBr mixture had been converted. A similar mixture was mixed (without grinding) and heated at 400° (below the fusion temperature) for eight hours. All four patterns were again present but the potassium bromide and sodium chloride patterns were not as intense as before, indicating a smaller amount of conversion. Another portion of the mixture was heated to 400° for thirty hours. In this case the potassium bromide and sodium chloride patterns were strong with only one or two lines of the potassium chloride and sodium bromide patterns, indicating almost complete reaction. It is interesting to note that no solid solution is formed between potassium chloride and potassium bromide or between sodium chloride and sodium bromide when heated at 400°, while when cooled from the fused state these two solid solutions are readily formed.

TABLE IV

SHOWING RESULTS FOR A 50–50 MOLE PER CENT. MIXTURE OF KCl AND NaBr GROUND TOGETHER

Line no.	d Obs.	$h\,k\,l$ indices	d for pure KBr	$h\,k\,l$ indices	d for pure KCl	$h\,k\,l$ indices	d for pure NaBr	$h\,k\,l$ indices	d for pure NaCl
1	3.28	200	3.28						
2	3.13			200	3.14				
3	2.975					200	2.970		
4	2.820							200	2.814
5	2.330	220	2.323						
6	2.225			220	2.220				
7	2.09					220	2.100		
8	1.988	311	1.981					220	1.990
9	1.89	222	1.897						
10	1.80			222	1.813	311	1.791		
11	1.711					222	1.715		
12	1.635	400	1.642					222	1.624
13	1.573			400	1.570				
14	1.469	420	1.469						
15	1.405			420	1.404			400	1.407

Tables V to VIII show the results obtained from a series of mixtures in case of which double decomposition was possible. In each case equilibrium was approached from both directions. The results shown in Table V indicate that potassium chloride and sodium fluoride do not unite with each other but that potassium fluoride and sodium chloride react completely to form potassium chloride and sodium fluoride.

TABLE V

$KCl + NaF \longleftarrow KF + NaCl$

Mixture no.		401	400
Comp., mole % 50–50		KF[a] and NaCl	KCl[a] and NaF
Phase I, cube edge = a	Obs.	4.618	4.624
	NaF	4.62	4.62
Phase II, cube edge = a	Obs.	6.260	6.268
	KCl	6.28	6.28

[a] Dry salts mixed and fused.

The results shown in Table VI indicate that potassium chloride and sodium iodide react to form potassium iodide and sodium chloride. Vaksberg[9] reports, as the result of a thermal investigation, that $KCl + NaI \longrightarrow KI + NaCl$ form an irreversible reciprocal system with equilibrium more nearly in the direction of $KI + NaCl$. Also potassium iodide and sodium iodide are

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(9) Vaksberg, *J. Russ. Phys.-Chem. Soc.*, **62**, 1259 (1930).

TABLE VI

$KCl + NaI \longrightarrow KI + NaCl$

Mixture no.		300	301
Comp., mole % 50–50		NaI[a] and KCl	KI[a] and NaCl
Phase I, cube edge = *a*	Obs.	7.061	7.056
	KI	7.052[b]	7.052
Phase II, cube edge = *a*		NaCl lines observed opposite the NaCl standard	

[a] Dry salts mixed and fused. [b] Clarke and Duane obtained a cube edge value of 7.064 Å. for potassium iodide.

reported to form a solid solution which does not show any break inside the reciprocal system. The results from Table VI would seem to indicate that the reaction goes to completion, since any unchanged sodium iodide remaining would influence the lattice dimensions of potassium iodide.

TABLE VII

$KCl + AgBr \longleftarrow KBr + AgCl$

Mixture no.		201	200
Comp., mole % 50–50		KBr[a] and AgCl	KCl[a] and AgBr
Phase I, cube edge = *a*	Obs.	6.280	6.284
	KCl	6.28	6.28
Phase II, cube edge = *a*	Obs.	5.746	5.740
	AgBr	5.750	5.750

[a] Dry salts mixed and fused.

The results shown in Table VII indicate that potassium chloride and silver bromide do not react but that potassium bromide and silver chloride react to form potassium chloride and silver bromide. Palkin,[10] using thermal methods, reports the shifting of equilibrium toward the formation of silver bromide. It is known that silver chloride and silver bromide as well as potassium bromide and potassium chloride form unbroken series of solid solutions. The patterns of pure potassium chloride and silver bromide reported in the table indicate complete reaction.

TABLE VIII

$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl$

Mixture no.		100	102
Comp., mole % 50–50		$NaNO_3$[a] and KCl	KNO_3[a] and NaCl
Phase I, cube edge = *a*	Obs.	5.628	5.626
	NaCl	5.628	5.628
Phase II, cube edge = *a*		Phase II in each case was found to be KNO_3 by direct comparison with KNO_3 lines	

[a] Dry salts mixed and fused.

The results shown in Table VIII show that potassium chloride and sodium nitrate react to form $KNO_3 + NaCl$. The behavior of this mixture is well known in aqueous solution, having been the subject of numerous investigations.[11]

Table IX indicates the direction of the halide reactions described above and lists the respective cube edges of the components involved. It is to be seen from the table that the reactions go in each case in such a direction that the average cube edge becomes a minimum. The average molecular volume becomes a maximum at the same time. Mathieu and Paić[12] have examined a series of reactions occurring in the solid state by means of the x-ray spectrograph and report that of seven reactions examined three take place with increase in molecular volume, two with a decrease and one with no change. The reactions examined were not double decomposition reactions. Berketoff[13] examined chlorides and iodides of Li and Na, Li and K, Li and Cs, Na and K, Na and Cs and K and Cs by an indirect method which involved the heat of solution of salt mixtures which had been melted together and those which had been merely mechanically mixed. From these studies Berketoff concluded that double decomposition occurs among these salts in such a direction that cations and anions of higher atomic weights unite with each other and cations and anions of lower atomic weights likewise unite with each other. All of the double decompositions described in the tables above check with this conclusion without exception. The reaction $AgCl + KI \longrightarrow AgI + KCl$ has been examined by Rostkovskii,[14] the reaction $TlNO_3 + KI \longrightarrow TlI + KNO_3$ by Palkin[15] and the reaction $TlNO_3 + KBr \longrightarrow TlBr + KNO_3$ by Rostkovskii,[16] thermal methods having been used in all three cases. These cases all check with Berketoff's conclusion.

TABLE IX

$KCl + NaBr \longrightarrow KBr + NaCl$

$6.28 + 5.94 = 12.22;\ 6.57 + 5.628 = 12.208$

$KCl + NaI \longrightarrow KI + NaCl$

$6.28 + 6.46 = 12.74;\ 7.052 + 5.628 = 12.680$

$KCl + NaF \longleftarrow KF + NaCl$

$6.28 + 4.62 = 10.90;\ 5.328 + 5.628 = 10.956$

$KCl + AgBr \longleftarrow KBr + AgCl$

$6.28 + 5.750 = 12.03;\ 6.57 + 5.540 = 12.11$

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(10) Palkin, *Acta Univ. Asiae Mediae*, Series VI, Chem. No. 4, 3–17 (1930).

(11) Uyeda, *Mem. Coll. Sci. Eng. (Kyoto)*, **2**, 245–259 (1910).

(12) Mathieu and Paić, *Compt. rend.*, **192**, 416–418 (1931).

(13) Berketoff, *Mitt. d. Akad. d. Wiss.*, **18**, No. 5 (1903).

(14) Rostkovskii, *J. Russ. Phys.-Chem. Soc.*, **61**, 595 (1929).

(15) Palkin, *ibid.*, **62**, 57 (1930).

(16) Rostkovskii, *ibid.*, **61**, 89 (1929).

Bergmann[17] has made an extensive study of mixtures of mercury and cadmium halides with Ag, Tl, NH_4, Li, Na and K nitrates, using thermal methods. This study is interesting because of the low ionization of mercury and cadmium salts. Bergmann concludes that in the case of the mercury halides almost no double decomposition occurs but that the cadmium halides show a tendency toward double decomposition in case no complex compounds are formed.

Summary

1. X-ray patterns have been determined for a series of mixtures containing KCl–NaBr, KCl–NaF, KCl–NaI, KCl–$NaNO_3$ and KCl–AgBr.
2. Evidence of double decomposition in the absence of a solvent has been obtained for mixtures containing KCl–NaBr, KCl–NaI and KCl–$NaNO_3$.
3. Equimolar mixtures of KF–NaCl have been shown to go to KCl and NaF when melted and equimolar mixtures of AgCl–KBr have been shown to form AgBr and KCl when melted.
4. KCl–NaBr mixtures have been examined below the fusion temperature and double decomposition found to occur.
5. Within the limit of error all double decompositions examined have been found to go to completion and the final products to be insoluble in each other in the solid state.

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[17] Bergmann, *Z. anorg. allgem. Chem.*, **157**, 83 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Some Chemical Reactions Involving Active Nitrogen[1]

BY R. H. EWART AND W. H. RODEBUSH

In the course of some investigations of the reaction of atomic hydrogen with hydrogen bromide a yellow luminosity was observed which was finally discovered to be due to traces of nitrogen present in the hydrogen which passed through the electrodeless discharge. In order to confirm this, hydrogen bromide at low pressure was introduced into a tube through which glowing nitrogen likewise at low pressure was flowing. The point of introduction of the hydrogen bromide was about 30 cm. from the discharge bulb. The nitrogen used in the experiment contained a trace of water vapor and the afterglow was quite brilliant and extended with no apparent diminution in intensity from the electrodeless discharge bulb to the liquid air trap.

At the point where the hydrogen bromide was admitted the afterglow became a brilliant orange of greatly increased intensity and all afterglow ceased in the tube below the point of admission of the hydrogen bromide. After a few minutes a white deposit appeared on the walls of the tube at the point of admission of the hydrogen bromide. The solid proved to be ammonium bromide and at the end of the run the liquid air trap was found to contain free bromine.

When the hydrogen bromide flow was stopped the brilliant orange flame diminished in intensity and moved at the rate of a few centimeters per minute. By the time the flame had moved some 20 cm. its intensity was apparently reduced to zero and the normal yellow afterglow suddenly swept through the apparatus as though a valve had been opened. When the flame was allowed to "die out" in this way no white deposit remained in the tube. In order to obtain samples of the white deposit it was necessary to stop the flow of active nitrogen at the same time that the flow of hydrogen bromide was stopped.

When hydrogen iodide is introduced in place of hydrogen bromide the same phenomena were observed and the flame was even more intense and of a brilliant blue color. With hydrogen chloride no effect was observed except that the afterglow ceased below the point of admission.

It is possible to offer a plausible explanation for this phenomenon. The ordinary bands in the nitrogen afterglow involve transitions from the 11th level of the B state to the 7th, 8th and 9th levels of the A state of the molecule. When the orange colored flame was examined with the spectroscope it was found to owe its color to strong bands of 5900–6000 Å. which probably correspond to transitions from the 9th level of the B state to the 6th or 7th levels of the A state.

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[1] For references to work on active nitrogen see Kneser, *Ergebnisse der exakten Naturwissenschaften*, **8**, 229 (1929); also publications by Kaplan in *Phys. Rev.* (1931–1932).