

TABLE II.—INFLUENCE OF TIME.

Run No.	Time. Hour.	Per cent. of nitrogen fixed.	Temperature C.
47	1/2	2.92	925
39	1	4.22	925
42 A	2	4.05	925
42 B	3	2.53	925
42 C	4	0.66	925

TABLE III.—INFLUENCE OF PRESSURE.

Run No.	Lbs. sq. inch pressure.	Per cent. of nitrogen fixed.	Time. Hour.
43	35	10.04	1
59	50	16.20	1
71	80	13.5	1

7. Conclusions.

The tables show, first, that more nitrogen is absorbed at a temperature of about 925° than at either higher or lower temperatures; second, that the maximum absorption is reached in one hour and that decreased values are obtained with either longer or shorter periods of heating; and, third, that about 50 pounds per square inch of nitrogen pressure gives the most efficient reaction.

The proportion of nitrogen fixed in the lithium compound does not differ greatly from that obtained commercially with "nitrolime," but the time necessary to so fix it is much less. The nature of the nitrogen compounds formed appears to differ considerably when lithium carbide is used from the compounds obtained when the nitrogen is absorbed in calcium carbide.

So far as the actual quantity of nitrogen so fixed is concerned, much better results might be anticipated with a purer carbide of lithium.

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THE HYDROLYSIS OF IODINE AND OF BROMINE. A CORRECTION.

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The values of the hydrolysis constants $(H^+)(I^-)(HIO)/(I_2) = 0.6 \times 10^{-12}$ and $(H^+)(Br^-)(HBrO)/(Br_2) = 2.4 \times 10^{-8}$, given in a recent article,¹ were calculated from the results of conductance measurements of saturated aqueous solutions of the halogens on the assumptions that

$(H^+) = (I^-) = (HIO) [= 4.0 \times 10^{-6}]$ and $(H^+) = (Br^-) = (HBrO) [= 0.0017]$.

Dr. Anton Skrabal, of the Technische Hochschule, Vienna, has kindly

¹ THIS JOURNAL, 32, 932 (1910).

pointed out by letter that owing to the presence of tri-iodide¹ a smaller value should have been taken for the concentration of iodide ion, and that therefore the value of the constant should be reduced to

$$(H^+)(I^-)(HIO)/(I_2) = 0.3 \times 10^{-12}$$

On account of a similar neglect of the effect of the presence of tri-bromide the above value of the hydrolysis constant for bromine is also much too large. According to Jakowkin² the "constant" $(KBr)(Br_2)/(KBr_3)$ equals 0.060 to 0.063 in dilute bromide solutions which are one-half to one-tenth saturated with bromine and increases slightly as the concentration of bromine decreases.³ The results of Boericke⁴ and of Worley⁵ in more concentrated bromine solutions show, however, that this "constant" decreases rapidly with increasing bromine concentration, and has no significance in saturated solutions. These authors advance the very probable explanation that polybromides higher than the tribromide are present, since the bromide concentration (which is calculated by difference) would then be too small if tribromide is assumed to be the only polybromide present. It therefore seemed improbable that the former conductance measurements in the saturated aqueous solution could be used in calculating the hydrolysis constant of bromine, and the following measurements in more dilute solutions were made.

The experimental methods were exactly the same as in the former investigation. The bromine was purified by shaking with conductivity water until the conductance of the saturated solution was practically the same as that formerly obtained. The dilute bromine solutions were freshly prepared in each experiment, and the concentration of each solution was determined before and after the conductance measurement. The concentration of the hydrogen ion was calculated from the specific conductance by taking, as before, the equivalent conductance of the acid to be 425. This number is probably too large, especially in the more concentrated solutions, since the conductance of the Br_3^- ion is undoubtedly smaller than that of the Br^- ion; but the error is small in the more dilute solutions, where the concentration of HBr exceeds that of HBr_3 . Furthermore, the conductance of the hydrogen ion is probably greater than at infinit dilution,⁶ which would tend to counterbalance the error due to the presence of tribromide. In the calculations the dissolved bromine which had not undergone hydrolysis was assumed to be present only as

¹ Compare THIS JOURNAL, 32, 924 (1910), Table V.

² *Z. physik. Chem.*, 20, 22 (1896).

³ Compare Jones, *J. Chem. Soc.*, 99, 402 (1911) and Joseph and Jinendradasa, *Ibid.*, 99, 280 (1911).

⁴ *Z. Elektrochem.*, 11, 64 (1905).

⁵ *J. Chem. Soc.*, 87, 1119 (1905).

⁶ THIS JOURNAL, 33, 792 (1911).

Br_2 and Br_3^- , and the concentration of Br^- was calculated from the relation $(\text{Br}^-)(\text{Br}_2)/(\text{Br}_3^-) = 0.063$.

The results are arranged in the following table in order of increasing bromine concentration. The data in the last line refer to the saturated solution, the conductance and concentration being taken from the former article.

CONDUCTANCE AND HYDROLYSIS OF AQUEOUS BROMINE SOLUTIONS.

Spec. cond. $\times 10^6$	Concentrations; Formula weights per liter $\times 10^3$.					
	Total Br_2	(H^+) = (HBrO)	(Br^-)	(Br_3^-)	(Br_2)	(H^+)(Br^-)(HBrO) / (Br_2)
261	31.4	0.616	0.415	0.201	30.6	5.2×10^{-9}
291	38.3	0.684	0.429	0.255	37.4	5.4×10^{-9}
287	38.5	0.675	0.423	0.252	37.4	5.2×10^{-9}
398	75.4	0.937	0.431	0.506	74.0	5.1×10^{-9}
503	115.8	1.184	0.422	0.762	113.8	5.2×10^{-9}
506	116.4	1.191	0.422	0.769	114.4	5.2×10^{-9}
545	125.1	1.283	0.434	0.849	123.0	5.8×10^{-9}
549	128.9	1.293	0.430	0.863	126.7	5.7×10^{-9}
727	210.0	1.71	0.40	1.31	207.0	5.7×10^{-9}

An examination of the table shows that the hydrolysis constant is

$$(\text{H}^+)(\text{Br}^-)(\text{HBrO})/(\text{Br}_2) = 5.2 \times 10^{-9}.$$

The results are unexpectedly concordant, but the conductances in the second, seventh and eighth experiments appear to be one or two per cent. too high, and have been rejected, because the chief sources of error would lead to high values.

The increase of the hydrolysis constant with the concentration of bromine is probably due to the presence of a polybromide higher than HBr_3 , since this would cause the concentrations (given in the table) of Br^- and Br_3^- in these solutions to be too large but would have practically no effect on the concentration of Br_2 . Conversely, by assuming the hydrolysis constant to be 5.2×10^{-9} , the concentration of Br^- in the saturated bromine solution may be calculated. By assuming also that the higher polybromide is HBr_3 , the composition of the saturated solution is found to be approximately as follows: Bromide, 0.37×10^{-3} ; tribromide, 1.21×10^{-3} ; pentabromide, 0.13×10^{-3} (sum, 1.71×10^{-3}); bromine as Br_2 , 0.2068.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE CONSTITUTION OF MARCASITE AND PYRITE.¹

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Attempts have been made at various times to ascertain the state of

¹ For the details of this study consult the author's doctoral thesis, 1910.