XLV.—*The Absorption of the Halogens by Dry Slaked Lime.*

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Although the action of chlorine on slaked lime has been investigated so thoroughly, the action of bromine appears to have attracted but little notice. Berzelius (*Jahresber.*, 1832, **11**, 130) first observed that bromine reacted with slaked lime with formation of a reddish-brown product, now often called "bromine bleaching powder." If the constitution of this compound is assumed to be analogous to that of bleaching powder, it seems difficult to account for its peculiar colour. It is well known that many adsorption compounds, as in the case of iodide of starch, have remarkable colours, and it was suspected that the colour of bromine bleaching powder could be explained in a similar way. The results of experiments to be described later appear strongly to favour this supposition. When a solution of bromine in carbon tetrachloride is allowed to remain in contact with dry slaked lime until equilibrium is attained, the concentrations of the bromine in the lime and in the solution are connected by the well known exponential adsorption formula. Similar experiments were afterwards carried out with iodine and chlorine in order to compare their action with that of bromine.

Experimental.

Preliminary experiments showed that bromine was not absorbed by pure quicklime. The slaked lime used in the experiments was freshly prepared from pure quicklime, and dried, sometimes in a vacuum desiccator, sometimes at 110°.

When bromine dissolved in carbon tetrachloride is brought into contact with dry slaked lime, the latter gradually absorbs bromine and deepens in colour to a brick-red, the action being facilitated by frequent shaking. Equilibrium is reached in the course of a few hours, although a further very slight absorption of bromine is noticed for a much longer period. Such a slight absorption after the first equilibrium has been attained was observed by Davis in the absorption of iodine by charcoal (Trans., 1907, **91**, 1666), and he explains these results by assuming that adsorption takes place at the surface of the solid with a high velocity, after which there is a slow diffusion into the interior of the solid with the production of a solid solution. A similar explanation will be adopted here.

In the following experiment a series of stoppered bottles, each containing 1 gram of slaked lime and 100 c.c. of bromine solution, were allowed to remain, with frequent shaking, at the ordinary temperature. At the end of one hour the solution in the first bottle was analysed, and at known intervals successive bottles of the series were examined, the last bottle remaining for five days. The concentration of the solution is expressed by the number of c.c. of thiosulphate solution equivalent to the iodine value of 10 c.c. of the bromine solution.

Time.	Concentration of solution.	Time.	Concentration ot solution.
1 hour	46·6	5 hours	46·3
2 hours	46·5	6 ,,	46·3
3 ,,	46·4	26 ,,	46·2
4 ,,	46·5	5 days	45·5

The first equilibrium, therefore, is reached even at the end of one hour, whilst a further very slight absorption of bromine is observed after an interval of five days.

The effect of temperature on the absorption of bromine was found to be very slight, as can be seen by the following figures, which refer to two analogous experiments carried out at 0° and 16°:

Concentration of solution. at 16°	Concentration of solution. at 0°
46·8	46·4

There is therefore a slightly greater absorption of bromine at 0° than at 16°, but the effect of temperature is so small that it was evidently unnecessary to use a thermostat in the remaining experiments, which were consequently carried out at room temperature.

The experiments were conducted as follows: One gram of finely powdered slaked lime was weighed into a dry glass bottle fitted with a well ground-glass stopper, and 100 c.c. of a carbon tetrachloride solution of dry bromine (the solution being of known strength) were added. The carbon tetrachloride was previously dried over calcium chloride and distilled. A series of similar bottles was prepared, using the same amount of lime and bromine solution in each bottle, but varying the concentration of the bromine. The bottles were shaken frequently, and the concentration of the solutions determined at the end of twenty-four to forty-eight hours by filtering quickly through glass wool into a burette, running off 10 c.c. into potassium iodide solution, and titrating the liberated iodine with standard thiosulphate solution. The concentration of bromine in the lime was calculated from the strengths of the bromine solution originally taken and that after contact with the lime. The concentration of bromine in the solution is expressed by the number of c.c. of thiosulphate required for 10 c.c. of solution, whilst the concentration of bromine in the lime is given by the amount of thiosulphate equivalent to the bromine in 1 gram of lime. The results are calculated, unless otherwise stated, in terms of thiosulphate of such a strength that 10 c.c. of iodine solution (1 c.c. $= 0.01282$ I) $= 37.4$ c.c. of thiosulphate solution.

The first experiment gave the following results:

Concentration of bromine in solution.	Concentration of bromine in lime.
11·4	114·7
33·95	119·0
56·7	120·4
79·9	118·5
102·5	121·0

The concentration of bromine in the lime remained practically constant, whilst its concentration in the solution varied within wide limits. The most probable explanation of this fact would be that a chemical compound is formed, the amount of bromine added in the first bottle being more than sufficient to react with the whole of the lime. The molecular ratio of bromine to lime in the compound would be:

$$Br : Ca(OH)_2 = 1 : 4.4.$$

In order to study the absorption of bromine before this constant composition is reached, a second series of experiments was made with a fresh specimen of slaked lime and much weaker solutions of bromine, when the following results were obtained:

* Concentration of bromine in solution $= C_2$.	Concentration of bromine in lime $= C_1$.	$C_1/C_2^{\frac{1}{3}}$.
3·82	30·7	19·6
9·45	36·3	17·2
13·73	49·2	19·6
22·06	55·1	19·7
38·4	39·7	—

* This table has already been given in a preliminary communication (*Proc. Camb. Phil. Soc.*, 1910, **15**, 527), except that the numbers have been recalculated so as to be given in terms of the thiosulphate solution taken as the standard throughout this paper. The succeeding table appeared also in the above publication.

In this case the concentration of bromine in lime increases with the concentration in the solution, except in the last bottle of the series. The third column gives the numbers calculated from the expression C_1/C_2^n, in which the value of $n = \frac{1}{3}$. These numbers are sensibly constant, and this constancy may be explained either by assuming that bromine is in solid solution in the lime, or that it forms an adsorption compound. Here the first assumption is untenable, as in that case bromine would be dissolved in the lime in fractions of an atom (provided that bromine dissolves in carbon tetrachloride as Br_2—a most probable assumption, since iodine dissolves in the same solvent as I_2). It is concluded, therefore, that bromine and dry slaked lime form an adsorption compound.

In this series of determinations it will be noticed that after the concentration of bromine in the lime has reached the value 55·1, there is a sudden fall to 39·7 on further increasing the concentration of the solution. Later it will be seen that the amount of bromine adsorbed by lime reaches a maximum independent of the concentration of the solution (after this has reached a certain minimum value). Such maxima of adsorption have been observed also by Schmidt in his experiments on the adsorption of acetic acid by charcoal (*Zeitsch. physikal. Chem.*, 1910, **74**, 689). It is suggested that in the last experiment the figure 39·7 represents the maximum adsorption of bromine in lime, whilst the high value of the preceding concentration, 55·1, depends on a phenomenon akin to supersolubility, and may be termed "superadsorption." Even when the bromine is in the superadsorbed condition its concentrations in the solution and the lime obey the exponential formula $C_1/C_2^{\frac{1}{2}}=k$.

In both the preceding series specimens of lime were used which had been dried for two days in a vacuum desiccator. In the following series it was dried for four weeks.

Concentration of bromine in lime.	Concentration of bromine in solution.
2·5	22·7
6·85	26·4
11·7	35·4
15·65	33·3
25·35	31·3
34·85	34·2
44·0	34·6
53·6	33·5

When the concentration of the solution is very small, the bromine is adsorbed by the lime, as in the last series of experiments, but the amount adsorbed soon reaches a maximum independent of the further increase of concentration of the solution. At first sight it might be supposed that a chemical compound is formed, but a little consideration shows that if this were the case the concentration of the solution should remain constant, while the concentration of bromine in the lime should increase gradually and then remain constant when all the lime had been converted into the compound, after which the concentration in the solution could increase. Hence the above results really show that dry slaked lime adsorbs bromine, but that a limit is soon reached when the adsorption is a maximum;

thus in the first series of experiments, where this maximum was reached in the first bottle, an erroneous conclusion was drawn (namely, that the constancy of concentration of bromine in the lime was due to the formation of a chemical compound) simply because there was then no evidence of previous adsorption.

It is stated (*Ann. Reports*, 1910, **7**, 48) that Killby has shown that "bromine bleaching powder" contains bromine in three forms, namely, as bromide, hypobromite, and as bromine more loosely combined, most probably as perbromide, to which the compound owes its colour. The conditions under which the compound was formed are not stated, so that it is impossible to compare these results with those obtained by the author. In the author's opinion the experiments recorded above show that the colour of "bromine bleaching powder" is due, not to a chemical, but to an "adsorption" compound. With lime not specially dried bromine gives also bromide and hypobromite, and if the red product formed in the above experiments is shaken with a small quantity of water the colour quickly disappears, and a mixture of calcium bromide, hypobromite, and unchanged lime remains.

The molecular ratio of lime to bromine when the adsorption reaches a maximum is, in the last series of experiments, $Ca(OH)_2 : Br = 14{\cdot}9 : 1$. Here the lime had been dried for four weeks in a vacuum desiccator, whilst in the first series, when the lime was dried for two days only, the ratio was $Ca(OH)_2 : Br = 4{\cdot}4 : 1$, so that the composition of the product at maximum adsorption is greatly altered by traces of water.

The colour of the lime deepened from yellowish-red to dark brick-red as the concentration of bromine in it increased, until the maximum of adsorption was reached, when no further change in colour was observed.

Lunge and Schoch (*Ber.*, 1882, **15**, 1883) showed that iodine reacted with slaked lime suspended in water with the production of calcium hypoiodite and iodide. . Under the conditions used in the following experiments, which were carried out as previously described for bromine, this reaction did not occur, but iodine was absorbed by the lime with the formation of a dark violet product, the colour of which deepened as more iodine was taken up, until it became almost black.

Preliminary experiments, carried out like those with bromine, were made to show the influence of time on the absorption of iodine:

Time.	Concentration of solution.
1 hour	31·6
2 hours	31·5
3 ,,	31·5
4 ,,	31·4
5 days	31·1

The equilibrium is reached very quickly, but, as in the case of bromine, a further slight absorption due to diffusion into the lime can be detected.

The influence of temperature, as shown by the following figures, is seen to be very small:

Temperature	0°	17°
Concentration of solution......	29·3	29·1

The remaining experiments, therefore, were carried out at room temperature.

The first series was made with the same specimen of lime used in the last experiment with bromine. The following results were obtained:

Concentration of iodine in solution = C_2.	Concentration of iodine in lime = C_1.	$C_1/C_2^{\frac{1}{3}}$.
2·6	9·8	7·12
6·4	13·65	7·35
10·0	15·9	7·38
14·7	17·7	7·23
23·95	17·2	—
33·1	17·0	—

The phenomena observed in the case of bromine and lime reappear. The iodine concentration in the lime at first increases with the concentration in the solution, and these two concentrations are connected by the formula $C_1/C_2^n = k$, where n is one-third, as in the case of bromine. The iodine concentration in the lime reaches a maximum independent of further increase of concentration of the solution. There is to be noticed also a very slight "superadsorption."

The molecular ratio of lime to iodine at the maximum concentration is $Ca(OH)_2 : I = 29·1 : 1$, which is much less than the corresponding ratio $Ca(OH)_2 : Br = 14·9 : 1$ for the same specimen of lime.

Another series of experiments with a specimen of lime dried for two weeks in a vacuum gave the following results:

Concentration of iodine in solution = C_2.	Concentration of iodine in lime = C_1.	$C_1/C_2^{\frac{1}{3}}$.
1·5	10·1	8·81
3·05	19·86	13·76
5·24	22·9	13·20
7·43	26·3	13·50
12·04	30·5	13·32
16·65	34·0	13·33
21·26	37·5	13·53

With the exception of the first determination, the ratio $C_1/C_2^{\frac{1}{3}}$ is here remarkably constant.

Experiments were then made with dry chlorine and dry slaked lime under conditions similar to the former. Preliminary trials showed that from weak solutions of chlorine in carbon tetrachloride the whole of the chlorine was absorbed by the lime without any indication of adsorption phenomena. At first it was suspected that, as carbon tetrachloride contained carbon disulphide, the chlorine had been used in reacting with the latter according to the equation:

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

This reaction is stated to take place when dry chlorine and carbon disulphide are used. In these experiments, however, it was found that this reaction did not occur appreciably in three days, since a solution of chlorine in the impure carbon tetrachloride had the same iodine value at the beginning and at the end of this period. Moreover, the experiments were repeated with tetrachloride free from disulphide and with exactly the same results.

In the following series of experiments the slaked lime was dried for four weeks. The concentrations of chlorine are expressed in terms of the standard thiosulphate solution as with bromine and iodine.

Concentration of chlorine in the solution.	Concentration of chlorine in lime.
0·0	205·1
0·0	410·2
0·0	615·3
32·7	725·5
136·6	733·6
204·3	729·4

A phenomenon entirely different from that noticed in the case of bromine and iodine is observed. The concentration of the solution now remains constant (zero), whilst the concentration of chlorine in the lime increases until the latter concentration reaches a maximum, when the concentration of the solution can now increase without affecting the concentration in the lime. This points undoubtedly to the formation of a chemical compound, in which the atomic ratio $Ca:Cl = 1:1·46$.

Finally, the action of the three halogens on the same specimen of lime, which in this case was dried at 110°, was compared. The results were as follows:

Chlorine.

Concentration of chlorine in solution.	Concentration of chlorine in lime.
0·0	61·75
0·0	123·5
2·1	235·8
8·25	288·0
21·4	280·0
33·0	288·0

[25 c.c. I (1 c.c.=0·01222 I)=45·15 of thiosulphate solution] neglecting the third result of this series the atomic ratio Ca : Cl=1 : 1·13.

Bromine.

Concentration in solution $= C_2$	Concentration in lime $= C_1$.	$C_1/C_2^{\frac{1}{3}}$.
0·32	15·35	22·5
2·08	16·0	12·6
5·2	22·14	12·8
8·55	26·26	12·8
16·34	22·0	—

The molecular ratio at the maximum of adsorption is $Ca(OH)_2$: Br=20·5 : 1. A small "superadsorption" is again observed.

The molecular ratio of lime to chlorine at the maximum of adsorption, in the specimen of lime dried for four weeks in a vacuum, was $Ca(OH)_2$: Cl=1 : 1·46, whereas in the above specimen, dried at 110°, the ratio is 1 : 1·13. The corresponding numbers for bromine are 14·9 : 1 and 20·5 : 1; thus, whilst small differences in the dryness of the lime have comparatively little effect on the absorption of chlorine, the effect on the absorption of bromine is seen to be very great.

Iodine.

Concentration in solution $=C_2$.	Concentration in lime $=C_1$.	$C_1/C_2^{\frac{1}{3}}$.
0·202	1·55	2·64
0·464	2·51	3·25
1·10	3·30	3·20
1·76	3·85	3·19
3·10	4·80	3·19

Conclusions.

(1) When bromine dissolved in carbon tetrachloride is added to dry slaked lime, the latter adsorbs bromine until a maximum of adsorption is attained. In some cases a slight "superadsorption" is noticed. The colour of bromine bleaching powder is due to this adsorption product.

(2) The concentrations of bromine in solution (C_2) and in lime (C_1) before the maximum of adsorption is reached are connected by the equation $C_1/C_2^{\frac{1}{3}}=k$.

(3) The amount of bromine adsorbed by slaked lime depends on the dryness of the lime.

(4) Similar results were observed in the case of iodine and lime. The value n in the formula $C_1/C_2^n=k$ is one-third, as with bromine, but the constant k is different for bromine and iodine.

(5) For the same specimen of lime the molecular ratio of iodine

to lime at the maximum of adsorption is less than the corresponding ratio for bromine.

(6) Chlorine behaves quite differently from the other two halogens under the same conditions. Adsorption phenomena could not be detected, but the results indicate the formation of a chemical compound.

(7) Slight differences in the dryness of the lime have much greater effect on the absorption of bromine and iodine than on that of chlorine.

In conclusion, I wish to thank Dr. Fenton for suggesting this research, and for his interest and advice throughout.

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