IV.—*Examination of the Hydrous Constituent in Minerals.*

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IN a paper lately communicated to the Chemical Society, I endeavoured to show that an exact examination of the rate at which water was expelled from hydrated substances at any constant temperature, might teach us much as to the constitution of these bodies. One of the bodies examined was the mineral Gypsum, which has been found in three different states—first, in its most usual form as $Ca\ SO_4,\ 2\ H_2O$, or as it should be written $2\ Ca\ SO_4,\ 4\ H_2O$ as in selenite; second as $2\ Ca\ SO_4,\ H_2O$ in which three of the molecules of water have disappeared, as in certain un-named forms of Anhydrite; and third as $Ca\ SO_4$ as in Anhydrite. Now these three can also be obtained by artificial means; the second being found in steam boilers where the water is evaporated under pressure; so I made several attempts to obtain the other two possible hydrates, $2\ Ca\ SO_4,\ 3\ H_2O$, and $2\ Ca\ SO_4,\ 2\ H_2O$ by evaporating solutions under different pressures, but I could obtain no satisfactory results.

In examining the dehydration of selenite, I noticed that the rate at which most of the water was driven off was nearly constant till the compound $2\ Ca\ SO_4,\ H_2O$ was reached; but on plotting the numbers in a curve, it was seen that the rate at which the first molecule came off was greater than that of the other two; that is, that the decomposition $2\ Ca\ SO_4,\ 4\ H_2O—H_2O$ took place at a greater rate than $2\ Ca\ SO_4,\ 3\ H_2O—H_2O$, pointing to the facts that the compound left by the first of these reactions really has an existence, but as the second and third molecules came off at the same rate, that is, there was no break in the straight line representing their evolution, the compound $2\ Ca\ SO_4,\ 2\ H_2O$ has no existence. I consider these results as interesting as they are unexpected, because we should have considered the existence of that last compound probable as it contains just half the original amount of water, and an even number of molecules. Since the publication of these results, I have examined a large number of substances, and as some of them are natural minerals, I think this the proper place to discuss the results.

The first mineral of which a complete examination was made was opal, a good white specimen of this hydrate of silica of Sp. Gr. 2·125 being used. It was reduced to a very fine powder and a portion ignited to determine the total amount of moisture it contained, and the total loss was found to be 8·85 per cent., agreeing pretty well with the formula $3 SiO_2, H_2O$ which requires 9·09 per cent. A quantity of the substance was weighed out, placed in a drying tube, which was immersed in a water bath, and heated to boiling; a current of air dried by passing through several vessels of strong sulphuric acid was passed over the substance in the tube, and two U tubes containing pumice stone saturated with the same acid, were used to collect the evolved moisture, one being attached to the apparatus while the other was being weighed, by these means keeping the dehydration going constantly. The weighings were done every 5 minutes while the moisture came off with sufficient rapidity to make a difference of about a centigram in the tube, and at longer intervals as the rate became slower. The reason for not allowing more than a centigram to pass into a tube at one time is because when air is so thoroughly dried as it was before passing over the mineral, it has an extreme avidity for moisture, and if the vitriol coating the pumice stone becomes in the least degree weakened, the moisture is not absorbed. In some cases where the mineral or other substance was very difficult to dehydrate two tubes containing anhydrous phosphoric acid had to be placed (one before the air entered the drying tube, and the other before it passed out at the other end of the apparatus), in the circuit, because the slightest quantity of moisture in the air prevented it from dessicating the substance.

The following table gives the rate at which the water came off from the opal.

Time.	Grs per. cent.	
5 minutes	1·31 ,,	5·01 per cent.
5 ,, ...	1·28 ,,	
5 ,, ...	1·20 ,,	
5 ,, ...	1·22 ,,	
5 ,, ...	0·18 ,,	3·23 per cent.
20 ,, ...	0·72 ,,	
20 ,, ...	0·58 ,,	
20 ,, ...	0·61 ,,	
20 ,, ...	0·52 ,,	
20 ,, ...	0·60 ,,	
20 ,, ...	0·02 ,,	
Total 2 hrs. 25 Mins.	8·24 per cent.	

From these figures we see that about one half of the moisture came off at a definite rate of about 0·26 per cent. per second, but the other half at not much more than a tenth of that rate, or at a rate of 0·036 per cent. per second. The second portion seems low, the reason being that the whole of the moisture was not driven off, and if we add the difference between 8·85 and 8·24 to the second portion, we get 3·84 which brings it closer. If we plot these figures as in the curve, fig. 9, plate V, we obtain a broken line, and that break shows the position of a multiple proportion compound having the formula $6\ Si\ O_2\ H_2O$. That substance is known to exist in certain forms of opal, such as hyalite, but the above numbers give no evidence of those intermediate forms which are described by Klaproth and others. Now to see if these natural forms of Silica agree in constitution with the same substance formed artificially, two different specimens of hydrated silica were prepared, the first by passing silicon tetrafluoride into water, and the other by adding ammonia to hydro-fluo-silicic acid, and boiling. Both were well washed with hot water and pressed between cloths in a screw press, and the cakes so obtained reduced to powder, and allowed to get dry by exposure to moderately dry air. They were not placed under a desicator, because many substances lose most of their water by drying over oil of vitriol. In that manner, I obtained two fine white powders without having used any but natural evaporation for their preparation. Each of those specimens was treated like the natural silica, that is the total moisture estimated in one portion and the rate of dessication at 100 per cent. done in another.

The following tables give the numerical results, while the curves in the diagram show graphically the progress of the decomposition. The total amount of moisture in each case was for No. 1 55·48, and for No. 2 55·92. This agrees very well with the formula $Si\ O_2\ 4\ H_2O$, which requires 54·55 per cent. H_2O, the slight excess being owing to hygroscopic moisture. The rates were as follows :—

Rate.	No. 1. Per Cent.		No. 2. Per Cent.	
5	11·33	41.92.	12·17	42·99.
15	30·59		30·82	
20	8·13	8·13.	7·37	7·37.
20	0·80	4·06.	0·75	3·99.
25	0·87		0·80	
20	0·81		0·83	
20	0·80		0·79	
20	0·78		0·82	
Total 2 hrs. 25 m.	54·11		54·35	

It will be seen that the latter part of these figures agree very well with that obtained from the natural silica. The time taken for dehydration was by chance the same in the two artificial as in the natural substances, but the former were not dehydrated so completely as the latter. These figures point to the existence of some interesting compounds, which may be seen from the following table. The original silica may be represented by the formula $SiO_2 + 4\ H_2O$, or multiplied by 6 as $6\ SiO_2 + 24\ H_2O$, when the decomposition will be represented as follows:—

Decomposition.	Substance formed.	Loss.	
		Found.	Calculated.
$6\ SiO_2\ 24\ H_2O$—$18\ H_2O$	$=6\ (SiH_2\ O_4)$	42·45	40·90
,, —23 ,,	$=6\ SiO_2\ H_2O$	50·20	52·27
,, —24 ,,	$=\ SiO_2$	54·23	54·55

We see that only the last of these compounds agrees with the natural mineral, but it shows that artificially prepared silica has nearly the same properties as the natural substance, because the rates of dehydration are practically the same for similar stages of decomposition. The first portion of the mineral gave 0·26 per second, and the corresponding portion of the artificial 0·38; the second 0·036 and 0·040, the greatest difference being between the two first portions. I think, however, that this may be explained by supposing that the compound $3\ SiO_2\ H_2O$ exists in the artificial state as well as in the natural, and that the rate of 0·38 represents the average of the two decompositions $6\ SiO_2$, $6\ H_2O$—$4\ H_2O$, and $6\ SiO_2$, $2\ H_2O$—H_2O, which last is the first of the decomposition in the mineral. A more minute examination of the rate at this point would settle that question, and such I intend to make. Certain other minerals are in a forward state of examination, but as some points of the curves require revisal, I shall reserve the publication of the results for another paper. The compounds of silica shown by this method may be tabulated thus.

$6\ SiO_2\ 24\ H_2O$.
$6\ SiO_2\ \ 6\ H_2O$.
$6\ SiO_2\ \ 2\ H_2O$.
$6\ SiO_2\ \ \ H_2O$.