WATER OF CONSTITUTION AND OF CRYSTALLIZATION.

By W. W. Coblentz.

It is well known that many substances belonging to all classes of chemical compounds unite with water, forming combinations from which it may be expelled by the application of a greater or less degree of heat; and from the circumstance that many of these combinations are crystalline, the water is said to be present in the form of *water of crystallization*. It is generally supposed that the molecules of water exist in their entirety situated among the other molecules of the substance. "The compounds containing water of crystallization are usually denied the title of atomic compounds ordinarily applied to combinations of two or more elements in which the constituent atoms are associated in a single molecule, under the influence of the force which has received the name of chemical affinity, and in contradistinction are termed *molecular* compounds, being regarded as combinations of two or more separate molecules, *e. g.*, $CaSO_4 + 2H_2O$. This, although perhaps true of many compounds containing water of crystallization, is certainly not true of all, and notably the sulphates, which are only deprived of their water of crystallization by heating to a high temperature. The last molecule retained with such persistency was termed, by Graham, *water of constitution*, to distinguish it from water of crystallization.

"In the present state of our knowledge it is impossible absolutely to define the meaning of these terms, or even to say that there is an absolute difference between the so-called water of crystallization and water of constitution, and not merely one of degree."[1] To sum up, water of crystallization differs from combined water in that it does not belong to the molecular structure but only to the crystalline structure of the substance. Examples of substances contain-

---

[1] Encyclopædia Brittanica, 9th Ed., V., pp. 489 and 505.

ing water of constitution are sugar, and brucite, $Mg(OH)_2$, in which the O and the H atoms are supposed to be scattered about in the molecule, and do not unite to form H_2O until sufficient heat is applied to cause "combustion." There is considerable evidence that in many compounds the affinity is different for the different parts of the crystal water.[1] For example, ordinary alum, $AlK(SO_4)_2 + 12H_2O$, gives off five molecules of H_2O at 100°, and five molecules at 120°, while the last two molecules remain until heated to 200°. In the same manner in the sulphates of Mg, ($MgSO_4$, 7 H_2O), Zu, Fe, Ni and Co the last molecule of H_2O passes off at 200° to 300° C.

Another distinction between water of constitution and water of crystallization is that in compounds containing the former, after the water is expelled by application of heat, *e. g.*, mica, the residue *will not* take up water again, while in the latter water is taken up again. An example of the latter is copper sulphate, $CuSO_4 + 5H_2O$. On applying heat, the blue crystal becomes a crumbling white mass, which, if put in water or even permitted to stand in the air, absorbs water and resumes its blue color and crystalline structure.

We thus see that the question of the association of atoms of oxygen and of hydrogen in certain compounds is by no means a settled one. The purpose of this note is to call attention to data bearing on this subject.

The absorption spectrum of water has been found by Julius,[2] Paschen,[3] Aschkinass[4] and others. All observers agree in their location of large absorption bands at the wave-lengths 1.5 μ, 3 μ, 4.7 μ and 6 μ. No one questions their being due to water. The only investigation bearing on this subject, from the standpoint of infra-red absorption spectra, is that of Königsberger,[5] who studied the pleochroism of gypsum (selenite), muscovite and biotite mica, etc. The thickness of the plate of selenite was 2.57 mm., which was sufficient to cause complete opacity at 3 μ. As a consequence he could not emphasize the importance of his observations

---

[1] Graham-Otto, Lehrbuch de Chemie, II., p. 173.

[2] Julius, Verhandl. Konikl. Akad. Amsterdam, Deel I., No. 1, 1892.

[3] Paschen, Ann. der Phys., 53, p. 334, 1894.

[4] Aschkinass, Ann. der Phys., 55, p. 406, 1895.

[5] Königsberger, Ann. der Physik., 61, p. 687, 1897.

as much as they deserve. He does mention, however, that from the absorption band at 1.5 μ, which coincides with that of water, it would appear that in selenite $CaSO_4 + 2H_2O$, the water of crystallization does not seem different from ordinary water.

The present investigation deals with the infra-red absorption spectra of the minerals brucite, $Mg(OH)_2$ and selenite, $CaSO_4 + 2HO$, using a mirror spectrometer, a rock salt prism, and a Nichols radiometer.[1] The former contains the O and H in the form of water of constitution, while the latter has the H_2O present as water of crystallization. The reader may ask what right we have to discuss this question from the mere study of the absorption spectra of water and a few minerals like the aforesaid. My reply is that from an extensive study of organic compounds,[2] in which it was found that certain groups of chemical compounds have similar absorption spectra, this seems permissible. Then, too, these curves, considered in connection with those of Königsberger, seem conclusive evidence, in themselves, that water of crystallization and water of constitution are distinct.

WATER, H_2O.

The transmission curves of water, found by Aschkinass (*loc. cit.*), are given in Fig. 1. They show that in order to be able to penetrate the infra-red beyond 3 μ the film must be about .01 mm. in thickness.

The transmission curve for water, used as a comparison spectrum in the present work, is given in Fig. 3. The film was much thinner than these, and the 4.65 μ band has almost disappeared.

MICA.

The curves for the micas — muscovite, $H_4K_2Al_6Si_6O_{24}$, and biotite (contains iron) — given in Fig. 2, *b* and *c*, are due to Königsberger (*loc. cit.*).

The curves are so entirely different from those of water that one does not hesitate to say that the condition of the oxygen and the hydrogen atoms, which are scattered about in the molecule, combining to form a molecule of water on applying heat, is entirely different from the molecule of the water of crystallization in selenite.

The 2.9 μ band of muscovite mica, which lies close to the water band at 3 μ, can hardly be attributed to water for the simple reason

---

[1] Described in the PHYSICAL REVIEW, Vols. XVI. and XVII., 1903.

[2] Prelim. Report in Astrophys. Jour., 20, p. 207, 1904.

that there is no band at 1.5 μ. Then, too, the general transparency is entirely different.

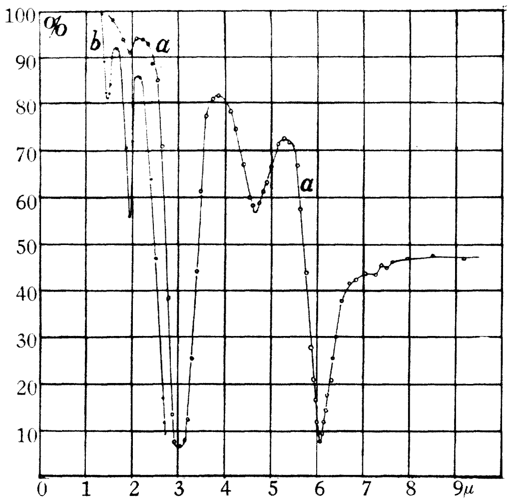

Fig. 1.

Transmission Curves for Water. Thickness of film: Curve $a = .01$ mm.; curve $b = .05$ mm.

The absorption of the biotite, in the visible spectrum, is due to the dark coloring matter, iron oxide, which it contains.

BRUCITE, $Mg(OH)_2$.

For this mineral as well as the selenite I am indebted to Professor Gill, of the Department of Mineralogy. Brucite is of especial interest on account of its OH-groups. It is also an illustration of water of constitution. On application of considerable heat the O and H atoms combine into, and pass off as a molecule of water, leaving as a residue the white MgO.

The brucite curve, *a*, Fig. 2, has but one large absorption band, at 2.5 μ, beyond which there are no bands until we arrive at 9 μ, beyond which point there is complete opacity.

This is but the second substance discovered which has an absorption band near the visible spectrum. The first one, beryl, $H_2Be_6Al_4Si_{12}O_{37}$, which has an enormous absorption band at .86 μ, was found by Königsberger (*loc. cit.*).

As a whole the curve of brucite shows that the OH-group, to the resonance of which numerous phenomena have been ascribed, by different investigators, cannot be very instrumental in causing the absorption bands of water. Also, from its dissimilarity with the water curve, one would infer that water of constitution is a different condition from water of crystallization.

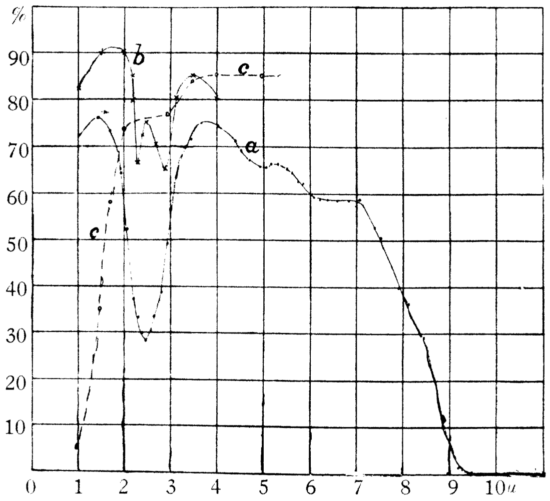

Fig. 2.

Curves *a* = brucite; *b* and *c* = mica.

SELENITE, $CaSO_4 + 2H_2O$.

Because of the great opacity of water, it is difficult to explore the absorption spectra of substances containing water of crystallization, unless the plates are very thin. Fortunately selenite can be split into folia of almost any desired thickness.

In the present work the selenite was of the massive variety which yielded thin, highly polished folia. In Fig. 3, curve *a* is due to Königsberger who used a plate 2.57 mm. in thickness, which prevented him from exploring the spectrum beyond 3 μ.

In the present work the plate was only .126 mm. in thickness and gave a very satisfactory curve, *b*. The absorption bands, at 1.5 μ, 2.95 μ, 4.6 μ and 6 μ, as well as the general absorption show a close resemblance to that of water. The band at 6 μ is somewhat obliterated by the increasing opacity of the plate which becomes opaque at 8 μ. Here the band of metallic absorption (reflection) begins, the maximum of which as determined by Aschkinass[1]

---

[1] Aschkinass, Ann. der Phys., 1, p. 42, 1900.

occurs at 8.69 μ. The comparison spectrum of water is given in curve *c*, which is for a film of water between fluorite plates. The plates were pressed together as close as possible in order to produce an unusually thin film. From the interference fringes, after the water had evaporated, the thickness of the film was estimated to be about .001 mm. This accounts for the absence of the small band at 4.65 μ, see Fig. 3.

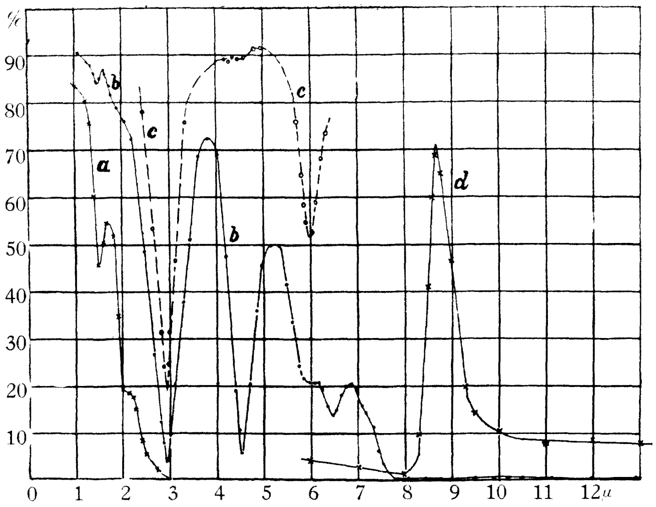

Fig. 3.

Curves *a*, *b* and *d* = selenite ; *c* = water.

The band at 6.5 μ coincides with the one for water vapor, found by Paschen at 6.5 μ.

The computed thickness of the layer of water contained in the .126 mm. plate of selenite is .059 mm., which explains the greater depth of the 4.65 μ band, and the greater opacity as compared with the water curve. The plate 2.57 mm. in thickness, curve *a*, represents a layer of water .12 mm. in thickness. We thus see a striking similarity between the curves for water and selenite.

The method of selective reflection seems better adapted for studying minerals far in the infra-red, especially compounds like alum, which has 12 molecules of water. In fact it seems the proper method for making an extensive study of minerals containing water of crystallization, since, with but few exceptions, they cannot easily be obtained in thin films.

As already indicated, the unusual similarity of the curve of selenite, and the great dissimilarity of the brucite and mica curves, to that of water, indicates that water of crystallization is not different from ordinary water. The whole shows that the difference between the so-called water of constitution and water of crystallization is more than "merely one of degree."

Physical Laboratory, Cornell University,
December 5, 1904.