SPECIAL ARTICLES

THE MODE OF REACTION OF HIGHLY INSOLUBLE OR UNDISSOCIATED SALTS

THE interesting note by Professor Smith[1] on the precipitation of metals by hydrogen sulfide has served to call again attention to our inability to explain the precipitation and reaction of highly insoluble or undissociated salts on the basis of reaction between simple ions. A result of the famous discussion of Haber[2], Bodländer[3], Abegg *et al.*, on the interpretation and consequences of the electrometric measurements of Bodländer on the silver cyanide complexes was the conclusion reached by him that in such cases the reaction is between the precipitating ion and the complex ion rather than with one of the ions into which the complex ion dissociates. Thus he proposed writing the reaction between potassium argentocyanide solution and sodium sulfide as

$$2\mathrm{Ag}(\overline{\mathrm{CN}})_2 + \overline{\overline{\mathrm{S}}} = \mathrm{Ag_2S} + 4\overline{\mathrm{CN}}$$

rather than

$$2\overset{+}{\mathrm{Ag}} + \overline{\overline{\mathrm{S}}} = \mathrm{Ag_2S}.$$

The necessity of an explanation such as proposed by Bodländer or Smith becomes apparent from several reactions of mercuric sulfide and mercuric cyanide. In the case of mercuric sulfide one finds that there is present but one mercury and but one sulfide ion in 1,000 liters, or 10^{-5} of an ion in 10 c.c. of solution. If we assume with Haber that the minimum time that an ion remains free is 10^{-18} second, it follows that at minimum intervals of 10^{-13} second, a Hg- and a S-ion flash through the solution. Yet if we have several grams of mercuric sulfide in 10 c.c. of water, addition of a KI solution of iodine will bring the mercury into solution as rapidly as it is added. The reaction in other words goes on billions of times as fast as can be predicted even on the implied assumption of Haber that electrons are transferred between atoms with a velocity of light (3×10^{-8} cm. being taken as the order of magnitude of the atom, and 3×10^{10} cm. is the velocity of light, or 10^{-18} second is the time of transfer of an electron or minimum time of existence of an ion according to Haber). It would therefore appear that the aforementioned reaction should also be considered as a reaction between the iodine and the molecules of mercuric sulfide on the surfaces of the precipitate as well as with any mercuric sulfide or hydrosulfide molecules momentarily present in solution.

Another interesting instance is the precipitation of mercuric sulfide by the addition of sodium sulfide to a solution 0.1 M. with respect to $\mathrm{Hg(CN)_2}$ and 1 M. with respect to KCN. From the dissociation value of 10^{-41} found by Sherrill[4] for the $\mathrm{Hg(CN)_4}$ complexion, it can be figured on the same assumptions as made above that in 10 c.c. of such a solution one Hg-ion flashes through the solution at minimum intervals of 10 seconds. Yet *precipitation* takes place rapidly.

Since the atomic theory is much more firmly intrenched now than it was at the time when Haber first raised the question as to the character of reactions of highly insoluble or slightly dissociated substances, we must disregard his first supposition that the atomic theory may be in error, and accept as a logical explanation his second supposition that molecules and complex ions take part in such reactions.

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1 *J. Am. Chem. Soc.*, 44, 1500 (1922).
2 *Zeit. f. Elektrochem.*, 10, 433, 733 (1904).
3 *Ibid.*, 10, 604 (1904).
4 *Zeit. f. phys. Chem.*, 43, 717, 735 (1903).

THE MUSCH RAIN-CORRECTING MOUNTING FOR POROUS PORCELAIN ATMOMETERS[1]

Two years ago Livingston and Thone[2] described "A simplified non-absorbing mounting for porous porcelain atmometers" which, by reason of its simplicity of construction and operation as well as its inexpensiveness, has since come into very general use. The essential feature of this mounting is a short column of mercury placed near the upper end of the straight glass feed-tube which connects the atmometer above with the water reservoir below. This column of mercury, held in place by two plugs of glass wool (one above and the other below), acts very effectively as a valve to prevent the passage of water from the atmo-

1 Contribution from the Osborn Botanical Laboratory.
2 SCIENCE, N. S., 52: 85-87, 1920.