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

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

rather than

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

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 $Hg(CN)_2$ and 1 M. with respect to KCN. From the dissociation value of 10^{-41} found by Sherrill[4] for the $Hg(CN)_4$ 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.

meter down the tube into the reservoir, at the same time having no effect whatever on the passage of water up the tube to replace that lost by evaporation.

Notwithstanding the obvious advantages of the Livingston-Thone mounting, there are certain objectionable features attendant upon its use which can not be overlooked. To begin with, the mercury valve with its glass wool plugs has to be properly constructed every time it is needed for use: once a season at any rate. Again, in sucking water through the tube, during the setting up of the apparatus, there is danger of drawing slivers of glass wool into the mouth. But perhaps the most serious objection has to do with the accumulation of air-bubbles in the atmometer or in connection with the glass wool plugs. It is impossible to detect bubbles in the atmometer except by taking the whole apparatus to pieces, while a bubble in the tube may sometimes become so large as to endanger the continuity of the water column.

The device to be described below was designed by Mr. Frederick Musch of New Haven as a result of experience in operating a series of porcelain atmometers for Dr. Norman Taylor—instruments equipped with the Livingston-Thone mounting. Like the latter,[3] the Musch mounting depends on a mercury valve to prevent the absorption of water, but here the resemblance ceases. The Musch device (Fig. 1, *A*) consists primarily of a J-shaped glass feed-tube, the straight end of which (*a*) extends up through the stopper of the reservoir while the curved end (*c*) passes down into the reservoir, reaching to within about half an inch of the bottom when in place. The atmometer is of course attached to the upper end of the tube, and a column of mercury (*Hg*) in the curve at the bottom of the J forms the valve. The short arm of the J is long enough to prevent the mercury splashing or being forced out of the tube into the bottle. A second important feature consists in a short side-arm (*b*), attached to the tube about an inch and a half above the bottom of the J and extending outward and upward. The outside width of the J and the outside distance between arm and tube are gauged to insure their easy insertion through the neck of the reservoir bottle. The side arm is attached at a point just high enough above the curve of the J to permit the latter to clear the bottom of the neck, while inserting, before the arm strikes the top. The side arm is long enough so that the straight part of it more than holds the mercury column, when desired, and at the same time short enough so that when in position it lies about half an inch below the shoulder of the reservoir bottle. The proper dimensions can readily be ascertained by the use of a cardboard model and a bottle of the type it is intended to use as the reservoir. The glass tubing should be of sufficiently large bore to permit the ready passage of large air bubbles.

In setting up the apparatus the feed tube is first shoved through the reservoir stopper from below and the atmometer stopper affixed to its upper end in the usual way. Next, enough mercury is placed in the crook at the bottom of the tube to completely block the passage. The whole thing is then carefully turned upside down, in such a way that the mercury column runs out of the J and into the side-arm. With mercury and tube in this position the atmometer, filled with water, is attached (or it can be attached empty and then filled either by suction or in the manner described below). The mount with attached atmometer is then turned right side up, the mercury resuming its

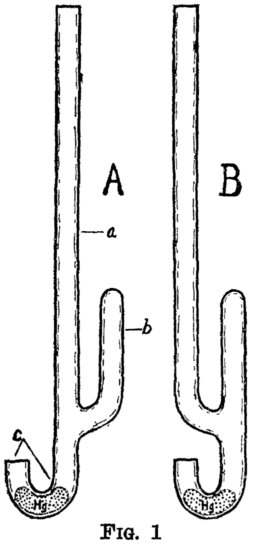

FIG. 1

[3] And like several others that had been described previously: see references in SCIENCE, 52, p. 86 (1920).

position in the crook of the J, the feed-tube is lowered into the reservoir, and the stopper is forced home. The filling of atmometer and tube is completed by turning the whole apparatus upside down and then alternately back and forth, in a manner which a little experimentation will readily suggest, due precautions being taken during this operation that the mercury retains its position in the side-arm. This same simple expedient is adopted at any time when it is desired to ascertain whether air bubbles are present in the atmometer and for getting rid of them. Any difficulty in persuading air bubbles to emerge from the atmometer into the feed-tube can be overcome by tapping the base of the instrument or by variously shaking the whole apparatus.

The Musch atmometer mounting has been thoroughly tested under various conditions, both by the writer and by others. It has already been adopted by several investigators for field work during the past season and appears to have given uniformly satisfactory results. The chief objection to which it may be open seems to be this: that during a heavy or protracted rain (or when left under a tap) there may be an initial absorption of water from without amounting to as much as 0.6 cc.[4] This absorption is due to the fact that the mercury valve does not remain stationary before the downward-pressing water column but retreats a short distance up into the short arm of the J. During a period when the weather at relatively brief intervals is alternately wet and dry it is conceivable that an error of several cc. might be introduced by the intermittent fluctuation back and forth of the mercury column; but ordinarily the error would be relatively inconsequential and could be corrected with reasonable accuracy if desired. The most obvious advantages of this style of mounting are (1) that it is possible to detect the presence of air bubbles in the atmometer by simply turning the whole apparatus upside down, and to get rid of them without even taking the cork out of the reservoir bottle; (2) that bubbles can not accumulate in the feed-tube; (3) that any objections which may arise from the use of glass wool are eliminated; and (4) that the mounting is always ready for immediate use. The contrivance can readily be made by any one adept at glass-working or it can be secured from at least one dealer in apparatus and supplies for about fifty cents.

[4] The amount of absorption may be greater if too short a column of mercury is used.

In conclusion, brief attention is called to a modification of the Musch mounting which has been devised by Dr. F. C. Gates (see Fig. 1, *B*). This modified model recommends itself in being somewhat easier to construct and somewhat more compact and also in the fact that the mercury runs more readily back and forth between arm and valve curve than in the original model. This latter feature, however, while of advantage in some respects, may prove a disadvantage when it comes to the rapid filling of atmometer and mount, except where this is done under water (the practise followed by Dr. Gates) or by the suction method: the replacement of long air columns and large bubbles of air is interfered with by the very ease with which the mercury slides back and forth.

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THE INDIANA ACADEMY OF SCIENCE

THE Indiana Academy of Science held its thirty-eighth annual meeting at Hotel Lincoln, Indianapolis, on Thursday and Friday, December 7 and 8, 1922. The officers of this meeting were as follows:

F. M. ANDREWS, Bloomington, *President.*
C. A. BEHRENS, LaFayette, *Vice-president.*
W. N. HESS, Greencastle, *Secretary.*
H. F. DIETZ, Indianapolis, *Assistant Secretary.*
W. M. BLANCHARD, Greencastle, *Treasurer.*
F. PAYNE, Bloomington, *Editor.*
F. B. WADE, Indianapolis, *Press Secretary.*

The meeting was unusually well attended and the program presented was as follows:

GENERAL SESSION

Estimating the wealth of Indiana as compared with other states. STEPHEN S. VISHER, Indiana University.

A photographic study of architectural acoustics. ARTHUR L. FOLEY.

Francis Galton, life and work. ROBERT HESSLER.

Paleolithic Stone Age in Indiana. S. FRANK BALCOM.