

soil are taken), that 17 per cent. of the sulphur trioxide was dissolved, results being obtained in closely agreeing duplicates. In a preliminary experiment it was observed that if the solution was only slightly acid (0.2 cc. excess of concentrated hydrochloric acid) iron in some form, probably an oxychloride, was frequently deposited on the bottom of the beaker in boiling prior to the addition of barium chloride, and stuck so tenaciously as to be removed only by the addition of considerably more hydrochloric acid. This same phenomenon was often observed in working with soils containing a moderately high percentage of iron with only a slight acidity of the soil solution.

In the experiment above to ascertain the solubility of barium sulphate in ferric chloride, 3 cc. excess of hydrochloric acid were present, as this was sufficient to prevent the deposition of iron and was found in a preliminary trial to exert an inappreciable, if any, dissolving effect.

Although the determination of sulphuric acid is not at present considered by soil chemists of the highest importance, because it generally exists in most soils in sufficient quantity for the complete development of crops for years to come, yet its importance as an essential constituent of plant food and its probable deficiency in many instances has prompted the writer to submit the above results and observations.

THE INTERACTION OF SULPHURETTED HYDROGEN AND ARSENIC ACID.¹

BY L. W. McCAY.

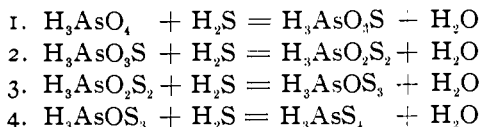
Received March 31, 1902.

FROM solutions of arsenic acid which have been treated with sulphuretted hydrogen I have been able to separate large amounts of monosulphoxyarsenic acid in the form of its tertiary sodium salt, and small amounts of disulphoxyarsenic acid, also in the form of its tertiary sodium salt. In addition to the above-mentioned acids the solutions appear to contain some trisulphoxyarsenic acid. Thus far, however, all attempts to isolate this compound have failed. If we assume its existence in the solutions, and a number of facts warrant us in making the assumption, the action of

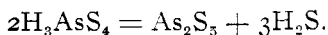
¹ The facts given in the first part of this article have been taken from a paper which appeared in the *Ztschr. anorg. Chem.*, **29**, 36 (1901).

sulphuretted hydrogen upon arsenic acid would appear to be in harmony with Ostwald's law of successive reactions (Gesetz der Reaktionsstufen). The successive stages through which arsenic acid passes during its transformation into sulpharsenic acid would then find expression in the following equations:

I. The sulphuretted hydrogen is always present in large excess.

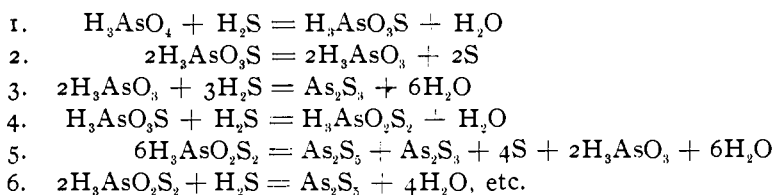


Since sulpharsenic acid cannot exist in the free state we have:



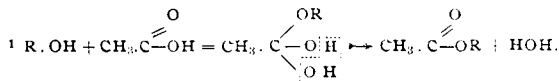
The sulphoxyarsenic acids, however, are unstable compounds and when the sulphuretted hydrogen is present in the solutions in but small amounts they break down partially, the monosulphoxyarsenic acid into arsenious acid and sulphur, the disulphoxyarsenic acid into arsenious acid, sulphur and the sulphides of arsenic. The sulphuretted hydrogen then converts the arsenious acid into arsenic trisulphide. Some arsenic pentasulphide is also formed according to I. We'll have then:

II. The current of sulphuretted hydrogen is slow or intermittent, so that the gas is not continually in excess:

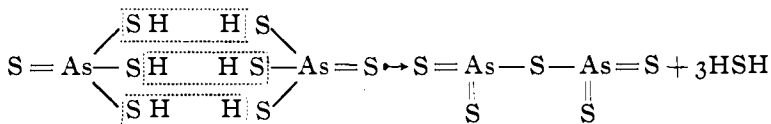
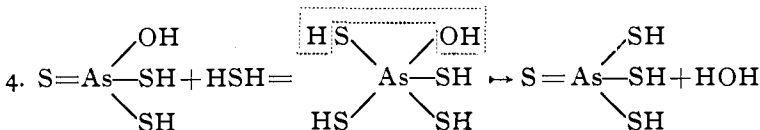
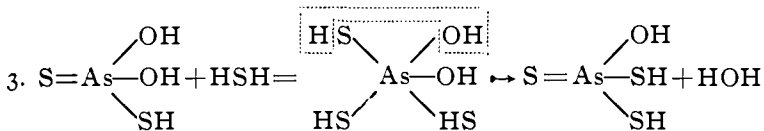
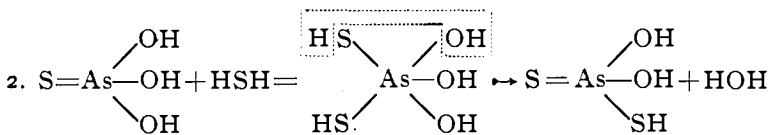
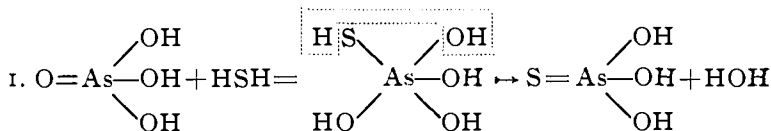


When, therefore, in these circumstances, the arsenic is all down, the precipitate will consist of a mechanical mixture of arsenic pentasulphide, arsenic trisulphide and sulphur, and this is in accordance with the facts.

The changes which occur when sulphuretted hydrogen acts on arsenic acid remind us forcibly of the reactions of organic chemistry. Are the former analogous to esterifications,¹ or are they



true ionic reactions? I firmly believe that they are ionic reactions, not simple but complex ionic reactions. However, to settle the matter beyond a doubt we need more facts. If the changes are additions and splittings, the mechanism of the various steps can be represented by the following equations:



Let us now endeavor to see if the electrolytic dissociation theory can be applied to an interpretation of the reactions.

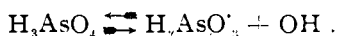
The various hydrogen atoms of a polybasic acid have different values as regards the strength of the latter. The first atom of hydrogen in a molecule of such an acid is always that of a stronger acid than the second, while the third and fourth follow in the same order. The first step in the dissociation of a polybasic acid is the most important one, and the amount of this dissociation depends upon the relative strength of the acid. Now since arsenic acid is a weak acid,¹ the dissociation which it undergoes when we dissolve

¹ According to Walden's measurements, it is about 20 per cent. dissociated in 0.1 molar sol.

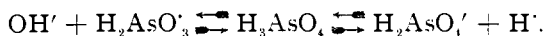
it in water will be necessarily small, so that the second and third steps in the breaking-down of the molecule can be neglected:



But since arsenic exhibits basic as well as acid properties, it seems reasonable to assume that arsenic acid can also undergo a slight basic dissociation. What has just been said in regard to the dissociation of a polybasic acid is correspondingly true of a polyacid base. The first step in the dissociation is the important one and since arsenic acid, if looked upon as a base, is undoubtedly a very weak one, the second and third stages in the cleavage of the molecule can be disregarded. The basic dissociation of the compound would be represented thus:



We may indicate both dissociations in this way:



The foregoing equation represents then, the equilibrium existing in an aqueous solution of arsenic acid. The $C_{(\text{OH}')}$ is extremely small, less even than the $C_{(\text{OH}')}$ in water, because, in general,

$$C_{(\text{H}')} \times C_{(\text{OH}')} = K$$

and if we increase the $C_{(\text{H}')}$ the $C_{(\text{OH}')}$ will correspondingly decrease. An aqueous solution of arsenic acid has a far greater value of $C_{(\text{H}')}$ than pure water, and hence a much less value of $C_{(\text{OH}')}$.

Again, consider the expression

$$C_{(\text{OH}')} \times C_{(\text{H}_2\text{AsO}_3')} = K_1 \times C_{(\text{H}_3\text{AsO}_4)}$$

Here the numerical value of K_1 is, of course, unknown, but even though it is undoubtedly very small, the value of $C_{(\text{H}_2\text{AsO}_3')}$ may still be appreciable, since the value of $C_{(\text{OH}')}$ is kept so extremely low by the considerable concentration of the H' ions.

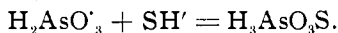
Allow the solution to be saturated and *kept* saturated with sulphuretted hydrogen,



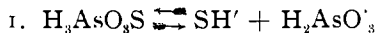
The degree of dissociation is slight, for sulphuretted hydrogen is a very weak acid. The dissociation, too, will be depressed to some extent by the hydrogen ions of the arsenic acid, seeing that arsenic acid is a stronger acid than sulphuretted hydrogen. It is

plain, however, that the $C_{(OH')}$ in the solution will be far less than the $C_{(SH')}$.

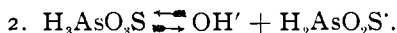
If, now, some SH' ions and some H_2AsO_3 ions unite, some undissociated monosulphoxyarsenic acid will be formed, the equilibrium of the system will be disturbed, more H_2AsO_3 ions will appear and more monosulphoxyarsenic acid will come into existence. In spite, therefore, of the very small value of $C_{(H_2AsO_3)}$ at the moment when the sulphuretted hydrogen is introduced into the solution, the resulting $C_{(SH')}$ value will soon become sufficiently great to occasion the production of a measurable amount of monosulphoxyarsenic acid,



Monosulphoxyarsenic acid is capable of undergoing two kinds of basic dissociation:



and



Since the SH' ions are far in excess of the OH' ions, the second kind of dissociation would probably predominate and since the solution is kept saturated with sulphuretted hydrogen, some H_2AsO_2S' ions will combine with SH' ions and some undissociated disulphoxyarsenic acid will be produced. The disulphoxyarsenic acid will, in its turn, yield $H_2AsOS'_2$ and OH' ions, and $H_2AsOS'_2$ and SH' will unite to form some trisulphoxyarsenic acid, and so on to the end.

The small ionic concentrations and the appearance and disappearance of the complex ions are quite in harmony with the sluggishness of the reactions, and a consideration of the rates of the various transformations would indicate the existence, at some time during the interactions, of a considerable concentration of monosulphoxyarsenic acid; later the maximum concentration of the disulphoxyarsenic acid, which, however, would be less than the maximum concentration of the former, and later still the maximum concentration of the trisulphoxy-compound, which indications are in accordance with the facts.

Now Brauner and Tomicek,¹ as well as Neher,² have shown that strong acids (HCl and H_2SO_4) accelerate, in a most pronounced way, the transformation of arsenic acid by means of sulphuretted hydrogen into sulpharsenic acid, so the question at once arises,

¹ *J. Chem. Soc.*, **53**, 145.

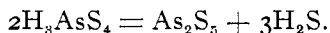
² *Ztschr. anal. Chem.*, **32**, 45.

What role do these strong acids play? In the light of what I have already said it is evident that the increase in the value of $C_{(H')}$, due to the presence of such acids, serves to decrease the value of $C_{(OH')}$ and so promotes the basic dissociation of the arsenic acid. These strong acids will, of course, lower the dissociation of the sulphuretted hydrogen, but we must remember that while the value of $C_{(SH')}$ undoubtedly falls off, that of $C_{(OH')}$ is reduced in a vastly greater proportion.

Given then an aqueous solution of arsenic acid, saturated and kept saturated with sulphuretted hydrogen, or given an aqueous solution of arsenic acid containing a considerable amount of a strong mineral acid (HCl) and saturated and kept saturated with sulphuretted hydrogen, and omitting any consideration of the second and third steps in the basic dissociation, we may represent the successive reactions in the following way:

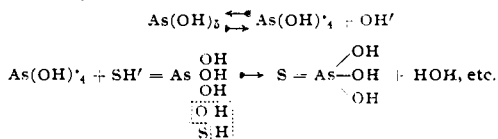
1. $H_3AsO_4 \rightleftharpoons H_2AsO_3 + OH'$
2. $H_2AsO_3 + SH' = H_3AsO_3S'$
3. $H_3AsO_3S \rightleftharpoons H_2AsO_2S' + OH'$
4. $H_2AsO_2S + SH' = H_3AsO_2S_2$
5. $H_3AsO_2S_2 \rightleftharpoons H_2AsOS'_2 + OH'$
6. $H_2AsOS'_2 + SH' = H_3AsOS_3$
7. $H_3AsOS_3 \rightleftharpoons H_2AsS'_3 + OH'$
8. $H_2AsS'_3 + SH' = H_3AsS_4$

The sulpharsenic acid then breaks down:



Neher¹ observed a number of years ago, and his results have been confirmed by Weinland² and myself,³ that when arsenic acid is present in a mixture of two volumes of strongest aqueous hydrochloric acid and one volume of water, sulphuretted hydrogen precipitates the arsenic almost instantly as the pentasulphide. If

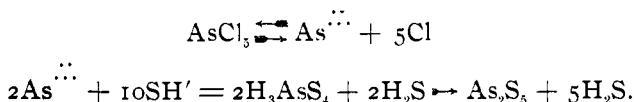
¹ Since the structural formula for monosulphoxyarsenic acid is undoubtedly $S = As(OH)_3$, it would, perhaps, be more rational to assume, in the solution, the presence of the normal compound $As(OH)_3$.



² *Ztschr. anal. Chem.*, **32**, 45.

³ *Ztschr. anorg. Chem.*, **14**, 44.

the rapid formation of the pentasulphide is in this case due to the $C_{(H)}$ then any strong acid which would give as great a $C_{(H)}$ as hydrochloric acid should have a similar effect, providing, of course, the anions occasion no disturbing by-reactions. Neher tried sulphuric acid and found that it acted in a manner analogous to hydrochloric acid. Nitric acid must be excluded but the behavior of other strong acids would prove interesting. There is, however, another way of looking at the matter. Assuming, as we have done, that arsenic acid can act as a very weak base, in the presence of a great excess of such a strong acid as hydrochloric acid, the production of the salt arsenic pentachloride¹ is at least not impossible. It would doubtlessly be formed by stages but the final product of the reaction we may assume to be the pentachloride:



If the train of reasoning above given be correct, the facts cited in my paper in the *Zeitschrift für anorganische Chemie* find a very satisfactory explanation in terms of the electrolytic dissociation theory.

In closing I wish to express my sincere thanks to Dr. George A. Hulett, of the University of Michigan, for his kindness in suggesting to me the possibility of arsenic acid undergoing a slight basic dissociation, as well as for the friendly interest he has shown in my work.

PRINCETON, N. J., February 1, 1902.

THE SOLUBILITY OF GYPSUM.

BY GEORGE A. HULETT AND LUCIUS E. ALLEN.

Received April 2, 1902.

ALTHOUGH the solubility of the substance $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been the subject of investigation by many careful workers, the results vary widely, while the experimental errors are comparatively small. The cause of these discrepancies was pointed out by Hulett,² in the course of an investigation of the influence of

¹ In this case we would have to assume that the aqueous solution of arsenic acid contains the normal compound H_3AsO_3 .

² *Ztschr. phys. Chem.*, **37**, 385.