entropy of fusion of chlorine, 9.5 entropy units, agrees well with the value found for the three tetrachlorides.

## Summary.

The specific heats of carbon, silicon, titanium and tin tetrachlorides have been measured from the temperature of liquid air to 298° K and, in addition, the specific heat of carbon tetrachloride was measured at still lower temperatures in order to determine the whole specific-heat curve for these compounds. The heats of fusion and, in the case of carbon tetrachloride, a heat of transition, were also determined, thus giving the total thermal content at 298° K.

The entropy of each of the compounds at 290° K and the entropy change in the formation of the compound from its elements have been calculated, and the results considered in reference to the mass of the atoms involved.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

# INDUCTION PERIODS IN REACTIONS BETWEEN THIOSULFATE AND ARSENITE OR ARSENATE:[1] A USEFUL CLOCK REACTION.

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Received October 26, 1921.

Vortmann[2] in 1889 obtained arsenious sulfide from arsenite or arsenate and thiosulfate in acid solution. Neither he nor any later worker in this field[3] mentions the reaction's sharp and highly reproducible induction period, though von Szilágyi says that the compound $K_3As(S_2O_3)_3$ which he obtained from arsenious chloride, potassium chloride and sodium thiosulfate "decomposes in water solution, in a shorter or longer time, according to concentration and temperature, and deposits $As_2S_3$."

Molal arsenite solution was prepared from sodium hydroxide and purest commercial arsenious oxide. Each portion used was converted to arsenious acid by the calculated volume of standard hydrochloric acid. Molal thiosulfate solution was standardized against iodine, purified, resublimed and dried. Standard solutions of hydrochloric and acetic acids were referred ultimately to properly dehydrated sodium carbonate.

Into one beaker we discharged from burets arsenite, water, neutralizing acid, and acetic or hydrochloric acid in excess; into a larger beaker,

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[1] The work on arsenates was performed mainly by O. J. Walker.

[2] Vortmann, *Ber.*, **22**, 2308 (1889).

[3] Weinland and Gutmann, *Z. anorg. Chem.*, **17**, 409 (1898). Gutmann, *Ber.*, **38**, 1728, 3277 (1905); **40**, 2818 (1907); **41**, 1650 (1908). Mackenzie and Marshall, *J. Chem. Soc.*, **93**, 1726 (1908). J. von Szilágyi, *Z. anorg. allgem. Chem.*, **113**, 75 (1920).

water and thiosulfate. All the volumes were planned to give the desired concentrations in a total volume of 100 cc. The two solutions, brought to 22.0°, were quickly and thoroughly mixed, noting the time by an ordinary watch, or by a stop-watch held by a second person if the period was short. The precipitate suddenly appeared from a clear solution after an interval fixed by temperature and concentration, which was carefully recorded. Table I gives induction periods in seconds with acetic acid in excess. These are inversely proportional to thiosulfate concentration over a wide range. They are almost independent of the other concentrations.

TABLE I

INDUCTION PERIODS WITH ACETIC ACID IN EXCESS

| *M* | HAc | Millimoles of Sodium Thiosulfate per Liter | | | | | |
|---|---|---|---|---|---|---|---|
| $H_3AsO_3$ Mmoles. | $S_2O_3$ Mmoles. | 800 Sec. | 400 Sec. | 320 Sec. | 240 Sec. | 200 Sec. | 80 Sec. |
| 20 | 4 | .. | 24 | .. | .. | 48 | 127 |
| 20 | 2 | .. | 25 | .. | .. | 50 | 130 |
| 80 | 4 | .. | 25 | 32 | 42 | .. | 130 |
| 80 | 2 | 13 | 25 | 33 | 45 | .. | 120 |
| 80 | 1 | .. | 27 | 32 | 47 | .. | 145 |

This reaction is highly suitable for lecture demonstrations both of induction periods and of the simplest relation between concentration and reaction velocity. The familiar reaction liberating iodine from iodate and sulfurous acid is less satisfactory, as its ingredients are less stable, and the time-concentration relations highly complicated.[4] The normal temperature coefficient of the induction velocity suggests another good experiment.

Vortmann gives the reaction: $2H_3AsO_3+9H_2S_2O_3=As_2S_3+3SO_2+9H_2O+3H_2S_4O_6$, while von Szilágyi finds, in concentrated solution, that $AsCl_3+3KCl+3Na_2S_2O_3=6NaCl+K_3As(S_2O_3)_3=6NaCl+3K_2S_3O_6+As_2S_3$. We have been unable to resolve either of the above reactions into stages which give the relations between time and reaction velocity observed by us. If the slowest stage is a unimolecular decomposition of thiosulfate, this must proceed in an unfamiliar fashion, as it is retarded by increasing hydrogen-ion concentration.

No analogy with the Landolt reaction, where the final product is for a time consumed by an original reactant, appears valid. This much, however, may be said,—the induction period is probably not a coagulation time effect, as it is not materially affected by excess of acetic acid, or by aluminum salts.

Table II shows that hydrogen ions beyond half the thiosulfate concentration greatly prolong the periods. Below this value, these are independent of acid concentration, hydrochloric or acetic. Arsenious sulfide,

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[4] Eggert, *Z. Elektrochem.*, **23**, 8 (1917).

then, forms less readily from thiosulfate decomposed by excess of hydrogen ion. Strangely enough, one mol of arsenite or arsenate will prevent 20 or more mols of thiosulfate from separating free sulfur when treated with large excess of hydrochloric acid.

The induction periods become somewhat longer if arsenate replaces arsenite. In general no sulfide appears unless there are over two mols of thiosulfate and of hydrogen for each mol of arsenic acid. Great excess of one reactant, especially of thiosulfate, compensates for deficiency in the other. Each curve in Fig. 1 represents a solution containing one constant concentration; in 1, 0.06 *M* $Na_2S_2O_3$; II, 0.05 *M* $H_3AsO_4$; III, 0.07 *M* $H_3AsO_4$; IV, 0.25 *M* $Na_2S_2O_3$; V, 0.14 *M* $H_3AsO_4$; VI, 0.02 *M* $H_3AsO_4$; VII, 0.25 *M* $H_3AsO_4$. Each point, located by trial, gives a concentration ratio yielding the barest turbidity after a long time. The area below and to the left of each curve includes all ratios which yield no precipitate.

TABLE II

EFFECT OF HYDROGEN ION ON INDUCTION PERIODS. TIME IN SECONDS

$H_3AsO_3$ constant at 80 millimoles per liter

| $Na_2S_2O_3$ per liter | HCl/$Na_2S_2O_3$ | | | | | | HAc/$Na_2S_2O_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Mmoles. | 4 | 2 | 1 | 1/2 | 1/4 | 1/8 | 4 | 2 | 1 |
| 400 | 240 | 120 | .. | .. | .. | .. | 25 | 25 | 27 |
| 320 | 300 | 120 | 60 | 35 | 30 | 30 | 32 | 33 | 32 |
| 280 | 360 | 210 | 125 | 42 | 33 | 34 | .. | .. | .. |
| 240 | 1260 | 780 | 150 | 50 | 40 | 40 | 42 | 45 | 47 |
| 80 | 3120 | 1500 | .. | .. | .. | .. | 130 | 120 | 145 |

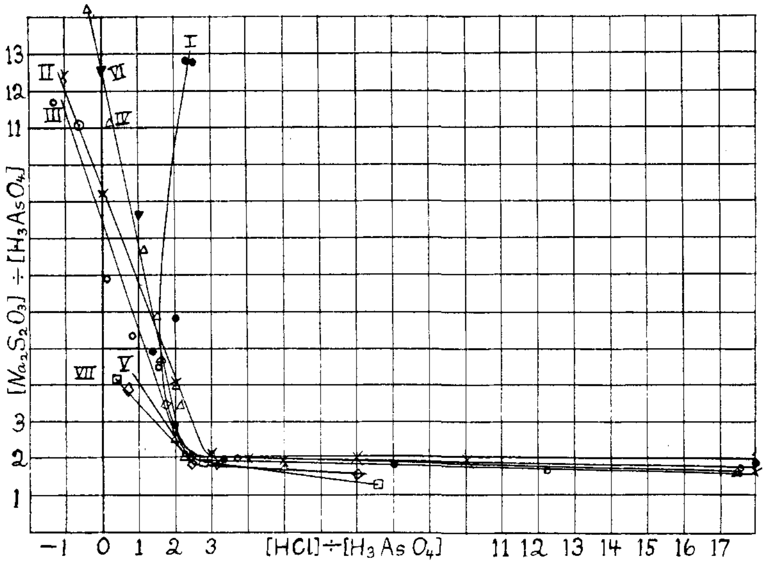

Fig. 1.

Mackenzie and Marshall state, without giving the evidence, that thiosulfate reduces arsenate to arsenite in acid solution. We may write the reaction

$$2S_2O_3'' + HAsO_4'' + 4H^{\cdot} = S_4O_6'' + H_3AsO_3 + H_2O.$$

In alkaline solution the reaction is reversed. We verified the above equation thus. In mols, Solution A originally contained 0.01000 $Na_2HAsO_4$, 0.02000 $Na_2S_2O_3$, and 0.04000 HCl. After standing for a long time only 0.00080 HCl remained. Solution B originally contained 0.01000 $Na_2HAsO_4$, 0.01500 $Na_2S_2O_3$, and 0.04000 HCl. The final excess of hydrochloric acid was 0.00892; *i. e.*, 0.03108 HCl has disappeared. If 0.01500 $Na_2S_2O_3$ uses up 0.00750 $Na_2HAsO_4$, 0.00250 $Na_2HAsO_4$ remains, which requires 0.00250 HCl to neutralize it. Therefore 0.02858 HCl was consumed in arsenite formation, very nearly the calculated amount.

After standing, solutions of Type A gave a copious and prompt precipitate with hydrogen sulfide as the equation would predict. But silver salts produced a yellow precipitate, rapidly darkening, and barium salts, added to the neutralized solution, an unstable white crystalline precipitate. The last two reactions, highly characteristic of trithionate, suggest the reversible reaction $H_3AsO_3 + S_4O_6'' \rightleftarrows 3H^{\cdot} + AsO_3S''' + S_3O_6''$. This equilibrium would be displaced from right to left by precipitation of arsenious sulfide, and from left to right by formation of insoluble trithionates. The speed of arsenite formation was studied in solutions containing 0.00500 $Na_2HAsO_4$, 0.01000 $Na_2S_2O_3$, and 0.02000 HCl in 100 cc. At the desired moment reaction was stopped by pouring into a quantity of alkali found by preliminary experiments to be nearly equivalent to the remaining acid. A small amount of standard acid or alkali completed the adjustment. The consumption of acid thus determined was after 15 seconds, 0.00972; 30 seconds, 0.01186; 1 minute, 0.01376; 2 minutes, 0.01504; overnight, 0.01847. The graph was obviously exponential in character, but the above data, before mathematical analysis, require correction at each stage for the quantities of acid hydrogen in the various anions present.

Thiosulfate, therefore, very rapidly reduces arsenate to arsenite, and then converts the latter into arsenious sulfide. These conclusions were confirmed by analysis of the precipitate.[5] The approximate equality of induction periods for arsenate and arsenite, allowing for acid and thiosulfate consumed in the first stage of the reaction, must follow; for

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[5] A brief preliminary statement regarding a part of this work in *Science*, **50**, 443 (1919), and *C. A.*, **14**, 3605 (1920) requires two corrections. (1) Freezing-point measurements, which we have since made but not recounted here, do not confirm the hypothesis of complex formation; the phenomena are sufficiently explained by the consecutive reactions which occur. (2) Vortmann was incorrectly quoted in the statement made there that arsenic pentasulfide is formed by the action of thiosulfate on arsenate.

a small concentration of arsenite, as shown previously, reacts almost as rapidly as a larger one.

The speed of precipitation of arsenious sulfide from arsenite was next studied (see Table III). To find the amount produced in 30 minutes for instance, the solution stood at 22° for $29^{1}/_{2}$ minutes from the end of the induction period. It was then quickly filtered through a weighed Gooch crucible, the operation consuming one minute. The sulfide was washed, dried at 110°, and after weighing treated with dil. ammonia to prove that free sulfur was absent, or present in traces only. The data are given in millimoles of $As_2S_3/2$. The course of the reaction suggests autocatalysis, but none of the *final* reaction products, added in small amounts to solutions at the start of their induction periods, changed these materially.

TABLE III

PRECIPITATION OF ARSENIOUS SULFIDE FROM ARSENITE

Millimoles per liter

(1) $H_3AsO_3$, 20; $Na_2S_2O_3$, 200; HAc, 400

| $t$ | $^{1}/_{2}$ | 1 | 2 | 4 | 8 | 16 | 432 | 3000 |
|---|---|---|---|---|---|---|---|---|
| $S$ | 6.36 | 7.11 | 7.80 | 8.50 | 9.63 | 11.38 | 16.23 | 21.6 |

Millimoles per liter

(2) $H_3AsO_3$,80; $Na_2S_2O_3$,80; HAc,160 m.

| $t$ | 1 | 2 | 4 | 8 | 16 | 404 | 3000 |
|---|---|---|---|---|---|---|---|
| $S$ | 2.32 | 2.63 | 2.82 | 3.18 | 3.45 | 6.26 | 18.0 |
| $S_1/S_2$ | 3.1 | 3.0 | 3.0 | 3.0 | 3.3 | 2.6 | 1.2 |

Vortmann's equation calls for 20.0 millimoles of $As_2S_3/2$ from Solution 1, and for 2/9 × 80, or 17.8 from Solution 2. The excess noted appeared to be due to free sulfur in each case. The precipitation reaction is to some extent reversible, as sulfurous acid dissolves the sulfide perceptibly, but this may be reprecipitated by blowing out sulfur dioxide with a stream of carbon dioxide.

Table IV shows how initial speeds of precipitation vary with concentrations. With acetic acid, speed is almost independent of arsenite, but nearly proportional to thiosulfate and to hydrogen *ion* concentration. With hydrochloric acid, however, the speed is, roughly, inversely proportional to the latter.

When the ratio of thiosulfate to arsenious acid, $Na_2S_2O_3/H_3AsO_3$, is 3, initial precipitation is much more rapid if most of the acid is added at the end of the induction period instead of at the beginning. When the ratio is 4, however, no difference is observed. See Table V. In Table VI it is evident that the same change in the ratio, from 3 to 4, strikingly abbreviates the induction period, especially in the more concentrated solutions. An explanation of these highly interesting observations would doubtless throw much light upon the reaction mechanism.

### Table IV

### Influence of Changing Concentrations upon Moles of $As_2S_3/2$ Precipitated in the First 15 Minutes

| $H_3AsO_3$ Mmoles. | $Na_2S_2O_3$ Mmoles. | HAc Mmoles. | $(H^+)$ Start | $As_2S_3/2$ Mmoles. | HCl Mmoles. | $As_2S_3/2$ Mmoles. |
|---|---|---|---|---|---|---|
| 80 | 200 | 400 | 0.0027 | 6.46 | ... | .... |
| 40 | 200 | 400 | 0.0027 | 6.08 | 400 | 9.08 |
| 20 | 200 | 400 | 0.0027 | 5.55 | 400 | 6.72 |
| 20 | 200 | 800 | 0.0038 | 8.21 | 800 | 3.36 |
| 20 | 200 | 200 | 0.0019 | 3.63 | 200 | 17.10 |
| 20 | 100 | 200 | 0.0019 | 1.93 | 200 | 5.37 |

### Table V

### Amount of Arsenious Sulfide Precipitated in 15 Minutes from End of Induction Period

Concentrations in millimoles per liter of final mixture

| | | | | | | |
|---|---|---|---|---|---|---|
| $H_3AsO_3$ | 80 | 80 | 80 | 80 | 80 | 80 |
| $Na_2S_2O_3$ | 320 | 320 | 320 | 240 | 240 | 240 |
| Initial HCl | 640 | 40 | 40 | 480 | 40 | 40 |
| Added[a] HCl | 0 | 600 | 1200 | 0 | 440 | 880 |
| Total HCl | 640 | 640 | 1240 | 480 | 480 | 920 |
| $As_2S_3/2$ | 12.8 | 12.6 | 6.8 | 9.0 | 6.7 | 3.2 |

[a] Added at end of induction period.

### Table VI

### Influence of Concentration Ratio upon Induction Periods

$HCl/Na_2S_2O_3 = 2$ in all cases

| $H_3AsO_3$ Mmoles. per liter | Ratio of $Na_2S_2O_3:H_3AsO_3$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 Sec. | 10 Sec. | 5 Sec. | 4 Sec. | $3^1/_2$ Sec. | 3 Sec. | 2 Sec. | 1 Sec. |
| 10 | 180 | 240 | 300 | 600 | 720 | 840 | 1120 | 1620 |
| 20 | ... | 180 | 180 | 360 | 540 | 720 | .... | .... |
| 40 | ... | 120 | 120 | 180 | 300 | 600 | 1110 | 1350 |
| 80 | ... | 65 | 120 | 120 | 210 | 780 | 1350 | 1500 |
| 100 | ... | ... | ... | 120 | 180 | 780 | 1380 | 1560 |

## Summary.

The induction period preceding precipitation of arsenious sulfide from an acidified solution containing thiosulfate and arsenite is extremely sharp and reproducible. Its duration is strictly in inverse proportion to thiosulfate concentration, and practically independent of concentration of arsenite, or of acetic acid. Hydrochloric acid prolongs the periods. It is much better for experimental demonstration of induction periods, of the relation between concentration and reaction velocity, and of the temperature coefficient of reaction velocity than the familiar iodine clock.

The prolongation of the periods by strong acids, the limiting concentrations yielding precipitates when arsenates are used, and the speed of precipitation were investigated.

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