observed. These apparently depend upon the nature of the negative ions present in solution.

Resistance measurements made by a. c. methods on glass electrodes indicate that most of the apparent resistance obtained by d. c. measurements must be due to polarization.

Large increases of apparent resistance of the electrodes result from drying processes even at room temperature, indicating the importance of water, or its ions, in conduction through the glass membranes.

Theories designed to explain the operation of glass electrodes are considered in the light of these new experimental results.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE EQUILIBRIA AND REACTION RATES FOR THE REACTION SODIUM ARSENITE–SODIUM TELLURATE[1]

BY PHILIP T. STROUP[2] AND VILLIERS W. MELOCHE

A preliminary study of the oxidation reactions of telluric acid and the tellurates revealed some reactions which seemed to be rather significant in the chemistry of tellurium. Among these, the reaction between sodium arsenite and sodium tellurate appeared to be particularly adapted to further study. This reaction was selected for the present research because of the convenient and reliable analytical methods involved and the absence of complicating side reactions. An examination of the existing literature showed that while numerous investigations have been reported on equilibria and reaction rates involving the arsenite–arsenate half reaction, no mention has been made of any reaction of arsenite and tellurate ions.

Materials

Telluric Acid.—The telluric acid was prepared by the Staudenmaier method[3] which depends on the chromic acid oxidation of tellurium dioxide in dilute nitric acid solution. After repeated crystallization the product was dried over calcium chloride. The resulting material was shown by analysis to be exceptionally pure H_6TeO_6.

Sodium Tellurate (Na_2TeO_4).—Sodium tellurate was prepared in solution by the addition of a standard solution of telluric acid to a solution containing an equivalent amount of carbon dioxide-free sodium hydroxide. This order of combination was used since the addition of sodium hydroxide to the telluric acid solution gave the difficultly soluble sodium acid tellurate. The strength of this stock sodium tellurate solution was checked by analysis.

Tellurium Dioxide.—Pure telluric acid was heated in a muffle furnace at 450° for twenty-four hours. The product obtained was pure white, formed a colorless solution with aqueous sodium hydroxide, and evolved no chlorine when treated with hydrochloric acid.

Sodium Tellurite (Na_2TeO_3).—A standard solution of sodium tellurite was prepared in a manner similar to the tellurate, by dissolving a weighed amount of tellurium dioxide in a known amount of concentrated, carbonate-free sodinm hydroxide solution. This solution was diluted to the desired volume with carbon dioxide-free water and the composition checked by analysis.

Arsenic Trioxide.—This oxide was obtained as the c. p., resublimed material and was resublimed once more. The product was pure white and dissolved in aqueous sodium hydroxide to give clear and colorless solutions. The degree of purity was determined by titration with standard permanganate solution and checked by titration with standard iodine solution.

Sodium Arsenite.—The sodium arsenite solutions of known concentration were prepared by dissolving weighed amounts of the arsenic trioxide in calculated volumes of standard sodium hydroxide solution necessary to prepare Na_3AsO_3. The strength of the solutions was checked by titration with standard iodine and blanks were run with each series of experiments.

Arsenic Acid and Sodium Arsenate.—Arsenic acid was prepared by nitric acid oxidation of arsenic trioxide. The product was repeatedly evaporated to dryness with nitric acid to insure complete oxidation and to drive off any oxides of nitrogen. The arsenic pentoxide formed was dissolved in water, the solution filtered and sodium hydroxide added in slight excess. The sodium arsenate which formed was allowed to crystallize and after separation from the mother liquor was purified by recrystallization. The product thus obtained gave no test for arsenite and melted at 85°. Analysis proved it to be $Na_3AsO_4\cdot12H_2O$.

Methods

Velocity measurements were made by pipetting definite amounts of the reactants, i. e., arsenite + tellurate or arsenate + tellurite, into large test-tubes, which were sealed or fitted with condensers if the temperature permitted. These tubes were then immersed in a constant temperature bath filled with oil maintained at the desired temperature. After definite intervals of time, the tubes were removed and immediately cooled. Each sample was broken open, the contents diluted with cold water and the solution made acid with hydrochloric acid. An excess of sodium bicarbonate was then added and the arsenite present titrated with standard iodine solution, approximately $N/20$. Since the reaction of iodine with tellurite was extremely slow,[4] it was possible to titrate arsenite in the presence of tellurite by considering the first appearance of the blue color as the end-point.

The constant temperature baths were maintained at temperatures of 89.6 (corr.) ±0.1, 101.1 (corr.) ±0.25, 110 ± 0.25 and 120 ± 0.25°.

Results

It had been noticed that arsenic trioxide and metallic arsenic were oxi-

4 B. Brauner, J. Chem. Soc., 59, 238 (1891).

dized by telluric acid, and that in alkaline solution the reaction was fast enough to be followed.   According to the reaction[5]

$$Na_3AsO_3 + Na_2TeO_4 \rightleftharpoons Na_3AsO_4 + Na_2TeO_3$$
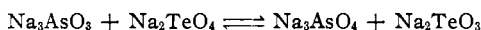
there were equimolecular quantities of the substances involved.   Therefore when the amount of arsenite was determined, the concentrations of the other substances could be computed by difference.   Using these results, it was found that uniform values were obtained when the velocity constant was calculated from the expression for a bimolecular reaction.   The reaction rate was expressed by

$$-\frac{dc}{dt} = k_1 \, (TeO_4^{--})(AsO_3^{---})$$

where the expressions in parentheses denote the stoichiometrical concentrations of the corresponding salts.   The values of k_1 were calculated by the integrated form

$$k_1 = \frac{2.3}{t(a-b)} \cdot \log \frac{b(a-x)}{a(b-x)}$$

Velocity Constant of the Direct Reaction.—The values of k_1 obtained at 89.6° (corr.) are shown in Table I.   The uniformity of the values of the velocity constant over such a range of time was taken as evidence of the bimolecular nature of the reaction.   The value of k_1 remained constant when the concentration of the arsenite varied from 0.05 to 0.0099 molar.

TABLE I

DIRECT REACTION RATES

Temperature, 89.6° (corr.)

Time, hrs.	AsO_3^{---} transformed, %	(a) Concn. TeO_4^{--}	(b) Concn. AsO_3^{---}	Mole transformed	k_1
2.2	60.0	0.05	0.0458	0.0275	0.00363
6	81.3	.05	.0458	.0372	.00342
10	87.9	.05	.0458	.0402	.00312
12	91.2	.05	.0458	.0417	.00353
25	96.1	.05	.0458	.0440	.00295
36	98.3	.05	.0458	.0450	.00321
4	71.5	.05	.0470	.0336	.00324
10	88.0	.05	.0470	.0414	.00340
24	94.6	.05	.0470	.0444	.00272
4	74.2	.05	.0247	.0188	.00263
4	69.4	.05	.0495	.0343	.00310
4	82.3	.05	.0099	.0081	.00264
				Mean value	.00293

It should be noted that the results presented were obtained from individual experiments and do not represent aliquots taken at successive time intervals.

[5] In examining the data it is important to note that these reactions were investigated at 89° and upwards and at these temperatures the solutions described are strongly alkaline.

The direct reaction rate was also measured at temperatures of 101.1 (corr.), 110 and 120°. The values of k_1 obtained by the same methods used at lower temperatures are given in Table II.

TABLE II

Temperature 101.1° (corr.)

Time, hrs.	AsO₃⁻⁻⁻ transformed, %	TeO₄⁻⁻	Initial concns. AsO₃⁻⁻⁻	k_1
4	80.0	0.0500	0.0495	0.00544
4	79.4	.0500	.0495	.00524
4	79.4	.0500	.0495	.00524
6	88.7	.0500	.0495	.00526
				.00529 mean

Temperature 110°

2	74.4	0.0500	0.0495	0.00793
4	83.4	.0500	.0495	.00681
4	85.4	.0500	.0495	.00781
12	94.4	.0500	.0495	.00713
24	97.2	.0500	.0495	.00684
				.00730 mean

Temperature 120°

4	90.4	0.0500	0.0495	0.01238

(Only one experiment was successful at this temperature)

Velocity Constant of the Reverse Reaction.—Velocity constants for the reaction arsenate + tellurite were obtained similarly to that used in the examination of the direct reaction. The values of k_2 shown in Table III were calculated by using the expression for a reaction of the second order.

TABLE III

REVERSE REACTION RATES

Temperature 89.6° (corr.)

Time, hrs.	Initial molar concn. AsO₄⁻⁻⁻	TeO₃⁻⁻	AsO₄⁻⁻⁻ transformed, %	k_2
47	0.0500	0.0245	0.50	1.21×10^{-6}
60	.0500	.0245	0.75	1.43
156	.0500	.0245	2.00	1.49
60	.0500	.0600	1.25	0.99
83	.0500	.0600	1.75	1.03

Equilibrium

As the direct reaction proceeded, a condition of equilibrium was reached in about one hundred hours. The extent of the reaction at equilibrium was most easily determined by allowing the reaction to proceed until no further change was produced by a longer time. This was done, using the technique already described. The resulting solutions were analyzed and the values given in Table IV.

TABLE IV

Initial concns. AsO$_3$ and TeO$_4$, 0.0500

Time, hrs	100	100	94	200	240	240	
AsO$_3$ transformed, %	98.0	98.1	97.9	98.1	97.9	97.9	Mean, 98.0

The mean of these results, 98%, was used to obtain the value for $K_{89.6}$, from the equation

$$K_{89.6} = \frac{(AsO_4)(TeO_3)}{(AsO_3)(TeO_4)}$$

where the terms in parentheses indicate the activities of the respective ions. Since no information regarding the activities was available, the analytically determined concentrations were used.

$$K_{89.6} = \frac{(0.980 \times 0.0500)^2}{(0.020 \times 0.0500)^2} = 2400$$

According to the law of mass action

$$K_{89.6} = \frac{k_1}{k_2} = \frac{0.00293}{1.26 \times 10^{-6}} = 2320$$

The two reaction velocities substituted in the above equation are mean values obtained from several determinations. The values for the equilibrium constant agree as well as might be expected in view of the lack of activity data.

The Arsenite–Tellurite Reaction.—In the presentation of data on the arsenite–tellurate reaction, no mention has been made of the possibility of a reaction involving arsenite and tellurite ions. Under the conditions of the experiments already described, the arsenite–tellurite reaction was exceedingly slow and was neglected altogether in calculating results. However, it should be noted that at greater concentrations of sodium hydroxide, arsenite and tellurite, the investigation of the main reaction would be accomplished with difficulty.

The Arsenite–Tellurate Reaction in Acid Solution.—Although it had been concluded from preliminary experiments that there was no reaction between arsenious and telluric acids in acid solution, further experiments in solutions containing 3 M sulfuric acid, arsenious and telluric acids indicated that there was an exceedingly slow reaction.

The Arsenite–Tellurate Reaction in the Presence of Added Sodium Hydroxide.—It was easily apparent that in the presence of added quantities of sodium hydroxide, the main reaction, arsenite + tellurate, proceeded at a much more rapid rate. However, no attempt is made here to present quantitative data. Our reason for this is that certain complications are involved. It has been mentioned that added quantities of sodium hydroxide not only accelerate the arsenite–tellurate reaction but also the previously negligible very slow arsenite + tellurite reaction. The final effect might be represented by the following reaction,

$$Na_2TeO_3 + 3Na_3AsO_3 \longrightarrow Na_2Te + 3Na_3AsO_4$$
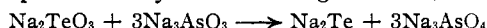
In the presence of air the Na_2Te is probably decomposed, giving elementary tellurium which in turn redissolves to produce the purple-colored solution of the polytelluride.

Temperature and the Velocity Constant.—That the velocity of a chemical reaction is accelerated by a rise in temperature is well known. In general, the rate of the reaction is doubled or even trebled for a rise of $10°$.
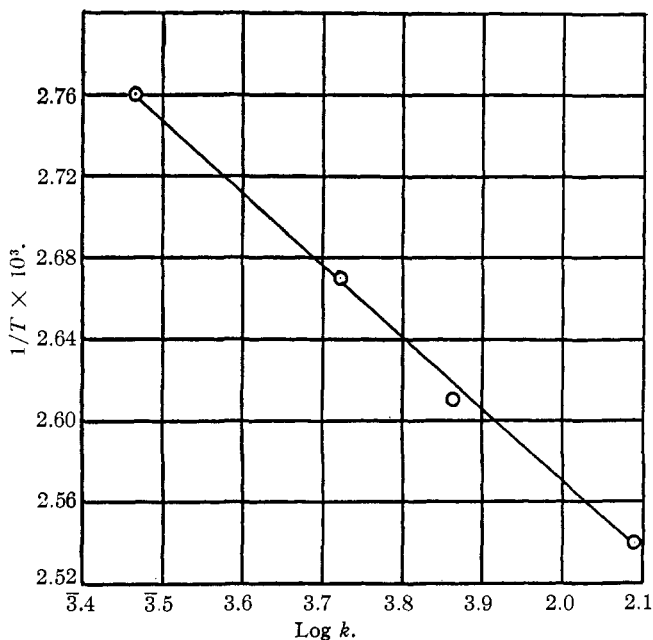

Fig. 1.—Effect of temperature on velocity.

A satisfactory expression for the relation between the velocity of a chemical reaction and temperature is that of Arrhenius in which

$$\frac{d \ln k}{d T} = \frac{E}{RT^2}$$

E representing the critical increment. The value for E may be obtained by plotting the reciprocal of the temperature, $1/T$, against $\log k$ and determining the slope of the line or may be calculated by substitution in the integrated form of the above equation.

<div align="center">GRAPHICAL METHOD</div>

| T	$1/T \times 10^3$	k	$\text{Log } k$
362	2.76	0.00293	$\overline{3}.466$
374	2.67	.00529	$\overline{3}.723$
383	2.61	.00730	$\overline{3}.863$
393	2.54	.01238	$\overline{2}.092$

$$m(\text{slope}) = \frac{\Delta y}{\Delta x}$$

or

$$\frac{3.164}{0.00022} = 14,380 = E$$

In considering the relative magnitude of E, it must be remembered that the reaction was studied at an elevated temperature.

Discussion

The reaction between sodium tellurate and sodium arsenite in aqueous solution under the conditions described in this communication

$$AsO_3^{---} + TeO_4^{--} \rightleftharpoons AsO_4^{---} + TeO_3^{--}$$
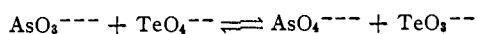
seems to be a relatively simple one, depending upon the fruitful collision of two ions, AsO_3^{---} and TeO_4^{--}. A preliminary consideration might lead one to believe that the reaction is more complicated. However, interpretation of the data already presented apparently supports the assumption that we were studying a bimolecular reaction. An application of the equations for a reaction of the second order to the analytical data obtained gives excellent velocity constants. It should be noted that the system probably is unique since there is no change in ionic atmosphere during the course of the main reaction, i. e., the reaction is initiated by bringing together AsO_3^{---} and TeO_4^{--} and during the reaction AsO_4^{---} and TeO_3^{--} are formed. A study of the reaction in an acid medium shows an almost negligible reaction rate while the study of the reaction in a system to which excess sodium hydroxide had been added indicates a relatively large increase in rate of reaction. This situation might be expected. In the acid solution the poorly dissociated arsenious and telluric acids would be present. If one associates degree of dissociation with rate of reaction, the reaction in acid solution would then be slow. In the study of the reaction in the presence of excess sodium hydroxide there may exist at least two possibilities. The hydrolysis of the strongly dissociated sodium salts might be repressed, thereby making available a greater propo.tion of free anions, AsO_3^{---} and TeO_4^{--}, for effective collisions or the excess hydroxyl ion might exhibit a strong positive catalytic effect, either case resulting in a decided increase in the rate of reaction.

Apart from these considerations, there is one added feature which might tend to make the reaction a relatively slow one. In passing from arsenite to arsenate and tellurate to tellurite, there must be, in addition to the usual electron transfer, the transfer of an oxygen atom. It is conceivable that a reaction involving the transfer of an oxygen atom would be measurably slower than one in which electron transfer takes place.

The arsenite–tellurate reaction under the conditions described in this paper is relatively free from side reactions and complicating analytical details. There are other inorganic reactions in which the effect of oxygen transfer could be studied. Unfortunately, many of them involve inter-

fering side reactions and the analytical problems seem almost incapable of solution.

The results of the present research might lead one to predict that many other slow inorganic reactions will be found if the investigations are made at high temperatures over long periods of time and providing suitable methods of analysis can be devised.

Acknowledgment

The authors wish gratefully to acknowledge the continued assistance of Professor Farrington Daniels throughout this research.

Summary

1. The reaction between arsenite and tellurate was studied at 90, 100, 110 and 120° and the rates of reaction were determined at different intervals of time for the direct and the reverse reactions.

2. Interpretation of analytically determined results using the expression for a reaction of the second order gave uniform values for the velocity constants.

3. The equilibrium constant was determined from the ratio of the concentrations of the anions at equilibrium and from the ratio of the velocity constants k_1/k_2. The two values for the equilibrium constant showed reasonable agreement.

4. While there was very little reaction between arsenite and tellurite in acid solutions, the rate of the reaction materially increased in alkaline solutions and in strongly alkaline solutions the speed of a previously ignored slow side reaction, arsenite–tellurite, increased to such an extent that the main reaction could no longer be studied quantitatively.

5. A qualitative study of the products of the side reaction which became prominent in the strongly alkaline solutions indicated that the reaction might be represented by

$$Na_2TeO_3 + 3Na_3AsO_3 \longrightarrow Na_2Te + 3Na_3AsO_4$$
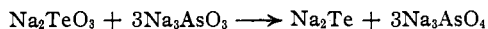
The purple-colored solution of polytelluride was the end product and was probably formed by the decomposition of Na_2Te and final solution of the elementary tellurium in telluride.

6. The critical increment was calculated by means of the Arrhenius equation and was found to be 14,380.

7. The relatively slow rate of reaction is attributed in part to the fact that the reaction involves oxygen transfer in addition to the usual electron transfer.

MADISON, WISCONSIN