water and alcohol. The velocities increase in the orders given.

2. The decompositions in water, and the decomposition of the sodium salt in alcohol, follow the first order law, but the decompositions of the anilinium salt in aniline and alcohol, and of the barium salt in alcohol, show an increase in the specific reaction rate as the decomposition proceeds. These departures have been explained on the basis of changes in the degree of ionization.

3. The reaction velocity has been shown to be dependent upon the concentration of the trichloroacetate ion. It is suggested that the reaction is a unimolecular decomposition of the trichloroacetate ion.

4. Temperature coefficients for the decomposition in the several solvents support the hypothesis that the stability of the ion is determined by the extent of solvation and the nature of the solvating substance.

5. The formation of chloride ion in solutions of trichloroacetates in water and alcohol has been shown to be the result of an oxidation of the chloroform which results from the decomposition of the trichloroacetates.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WORCESTER POLYTECHNIC INSTITUTE]

The Potentiometric Determination of Arsenates[1]

BY W. E. HANSON, S. B. SWEETSER AND H. B. FELDMAN

During the titration of acid arsenates with silver nitrate, the nitric acid formed in the reaction prevents the potentiometric determination of the arsenate since it reacts with the insoluble silver arsenate.

Bedford, Lamb and Spicer,[2] using as buffers sodium bicarbonate, ammonium acid succinate and sodium phenolphthalate found that no end-points could be secured. By means of a secondary titration with sodium hydroxide during which the acid formed in the reaction was destroyed, they were able to carry out the potentiometric titration successfully. In addition to requiring the use of two burets, the above method of conducting the titration is exceedingly tedious since the acid formed after each small addition of silver nitrate must be neutralized by addition of base.

In the following work, it was found that under the proper conditions the potentiometric determination of arsenates could be accomplished by using sodium acetate as a buffer.

Apparatus and Materials.—The cell used in this work was composed of a saturated calomel electrode connected to the solution being titrated by a bridge containing agar saturated with potassium nitrate. In this solution was immersed a silver electrode. The voltage of this cell was determined using a Leeds and Northrup student potentiometer.

All solutions used in this work were made from recrystallized C. P. salts and were standardized by standard volumetric and gravimetric procedures.

Experimental

The fact that Bedford, Lamb and Spicer[3] found in every case that more base was necessary for the titration than the amount theoretically necessary to neutralize the acid formed in the reaction suggested the addition of a large excess of free base before the titration with silver nitrate, thus eliminating the secondary titration. Accordingly, a series of experiments were carried out in which 1.5 to 3 times the theoretical amounts of sodium hydroxide necessary to neutralize the acid formed in the reaction were added to solutions of 25 cc. of 0.1004 *N* Na_2HAsO_4 which had been diluted to 225 cc. and these alkaline solutions were titrated with 0.1008 *N* silver nitrate. In every case it was found that the experimentally determined equivalence points indicated an amount of silver nitrate greater than that theoretically required, the deviation between the experimentally determined and theoretical equivalence points being about 2% when 1.5 times and about 4% when 3 times the theoretical amounts of base were used. The nature of these deviations indicated co-precipitation of silver oxide with the silver arsenate.

In order to avoid this precipitation of silver oxide and at the same time keep the hydrogen-ion concentration of the solution low enough to prevent the solution of the silver arsenate, it was decided to use sodium acetate as a buffer. A series of titrations was made in which the amount of acetate present corresponded to 2, 10, 50 and 100 times the amount necessary to react with the nitric acid formed in the reaction. The solutions containing 10, 50 and 100 times the theoretical amounts of acetate showed characteristic titration curves but the rate of change of voltage with addition of silver nitrate in the vicinity of the equiva-

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(1) The material presented in this paper is partly from the theses submitted by W. E. Hanson in 1932 and S. B. Sweetser in 1933 in partial fulfilment of the requirements for the degree of Bachelor of Science.

(2) Bedford, Lamb and Spicer, THIS JOURNAL, **52**, 583 (1930).

(3) Ref. 2, p. 587.

lence point was so small and remained of the same order of magnitude over so wide a range as seen by the data in Table I(a) that the determination of the equivalence point had to be made graphically by plotting cc. of silver nitrate used against the voltage and selecting the middle point of that portion of the curve having the maximum slope. Curve A of Fig. 1, which is plotted from the data secured using ten times the theoretical amount of acetate, shows the relatively small value of $\Delta E/\Delta$ cc. at the equivalence point. The effect of an increased amount of acetate consisted of a decrease in the voltage of the cell at the experimentally determined equivalence point as shown by curve B, which is plotted from the data secured using 100 times the amount of acetate necessary to react with the acid formed in the reaction. This, no doubt, was due to the decrease in the activity coefficient of the silver ion caused by the increase in the ionic strength of the solution.

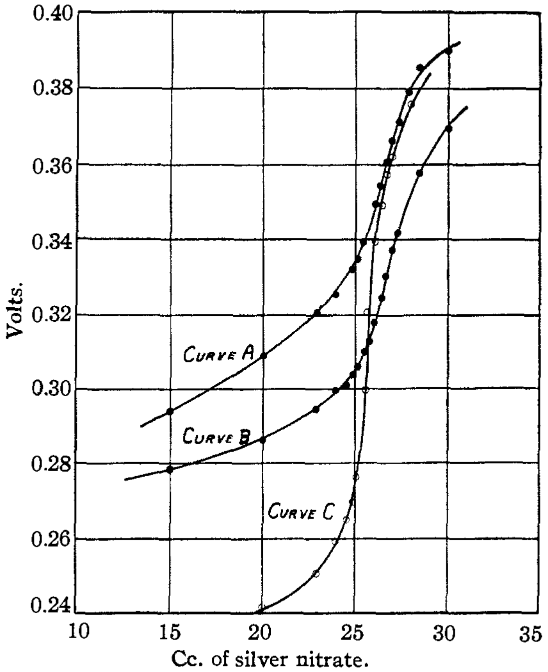

Fig. 1.—Curves A and B, water as solvent medium; Curve C, water–alcohol as solvent medium.

In order to increase the value of $\Delta E/\Delta$ cc. at the equivalence point and thereby increase the accuracy of determining it, a solution of alcohol and water was used as the solvent medium since in such a solvent silver arsenate would probably be less soluble than in water. Two titrations in which the amount of acetate present was, respectively, 10 and 100 times equivalent to the acid formed in the reaction were carried out in a medium which consisted of approximately 50% ethyl alcohol by volume at the equivalence point. As seen from the data in Table I(b), a satisfactory equivalence point could be determined by the method of selecting the maximum $\Delta E/\Delta$ cc. point. Ten times the theoretical amount of acetate necessary to react with the acid formed in the reaction was found to be the optimum amount of buffer to use since more than this caused a decrease in the value of $\Delta E/\Delta$ cc. at the equivalence point. Equivalence points determined in the above manner agreed with the theoretical to the extent of less than 1%.

Table I

(a) Using 10 × Theoretical Amount of Acetate. Water as Solvent. Total Volume of Solution at E. P. = 250 cc.

$AgNO_3$, cc.	Potential, m. v.	E/cc.
24.00	332.0	
25.20	334.7	9.0
25.50	338.5	12.9
25.80	342.5	13.3
26.10	348.5	20.0
26.40	354.2	19.0
26.70	361.0	22.7
27.00	366.0	16.7
27.30	371.0	16.7
27.90	379.0	13.3

Experimental Eq. Point = 26.20 cc.
Theoretical Eq. Point = 25.43 cc.

(b) Using 10 × Theoretical Amount of Acetate. Alcohol = 100 cc. Total Volume of Solution at E. P. = 200 cc.

$AgNO_3$, cc.	Potential, m. v.	E/cc.
24.00	259.8	
24.60	265.0	9
24.90	269.5	15
25.20	276.2	22
25.55	299.0	65
25.80	321.0	88
26.10	338.0	57
26.40	349.5	38

Experimental Eq. Point = 25.67 cc.
Theoretical Eq. Point = 25.43 cc.

Figure 1, on which are plotted the data secured using 10 × the theoretical amount of acetate with water in one case (curve A) and a solution of alcohol and water in the other (curve C), shows clearly the effect of alcohol on the titration curve. A comparison of the two curves shows a much larger slope in the vicinity of the equivalence point in the case of the alcohol–water solution.

Solutions of higher alcohol concentration were tried but it was found that the potential decreased slowly with time, this being due probably to the decrease in the rate of the precipitation reaction caused by the substitution of alcohol for water in the medium in which precipitation occurs. In the case of solutions containing less than 50% alcohol by volume, the titration curves decreased in slope in the vicinity of the equivalent point with decrease in alcohol concentration so that the accurate determination of the maximum $\Delta E/\Delta$ cc. point became impossible.

In order to determine the effect of dilution on the accuracy of the determination, experiments were performed in which 15 cc. of arsenate solution was used instead of 25 cc. and the total volume at the equivalence point was made 500 cc. instead of 200 cc. as was the case with the titrations given in Table I (a) and (b). In spite of this dilution a definite maximum $\Delta E/\Delta$ cc. point could be detected and the agreement between the observed and the theoretical equivalence points was about 1.5 parts per 100.

In order to determine the commercial applicability of the above potentiometric method the arsenate content of a commercial sample of calcium arsenate was determined volumetrically and potentiometrically in the following manner. The volumetric determination was made by reduction of the arsenate to arsenite followed by subsequent oxidation of the arsenite by standard iodine solution. The potentiometric method consisted of an adaptation of the method used by Bedford, Lamb and Spicer,[4] in which the titration was made after the addition of buffer and the required amount of alcohol.

Due to the relatively high ionic strength of the solution treated as above, the maximum value of $\Delta E/\Delta$ cc. was found to be about 25 millivolts per cc. Nevertheless, the maximum was easily detectable. Two volumetric determinations gave as the As_2O_5 content of the sample 40.38 and 40.11%, respectively, while two potentiometric determinations showed 39.93 and 39.66% As_2O_5.

Summary

1. Using sodium acetate as a buffer it is possible to determine potentiometrically the arsenate content of acid arsenates.
2. The optimum conditions for the determination consist in using ten times the theoretical amount of acetate necessary to react with the acid formed in the reaction, in a solvent consisting of 50% alcohol by volume.
3. The potentiometric method of determination can be used for the determination of the arsenate content of a commercial sample of calcium arsenate.

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[4] Ref. 2, p. 588.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A Correlation of the Photosyntheses of Phosgene and Hydrogen Chloride

BY G. K. ROLLEFSON

The two photochemical reactions involving chlorine which have been most extensively studied are those with hydrogen and carbon monoxide to give hydrogen chloride and phosgene, respectively. In each of these systems it has been shown that the reaction proceeds by a chain mechanism consisting of a pair of reactions, one using up chlorine atoms and the other forming them. The number of chains started is determined by the number of light quanta absorbed and the chain length is determined by the relative rates of the reactions which result—directly or indirectly—in the elimination of chlorine atoms and the reaction which continues the chain. A study of the kinetics of the two systems has shown that the chain terminating reactions are different. That for the phosgene reaction involves COCl and Cl[1] whereas the hydrogen chloride reaction requires a reaction of Cl atoms at the wall or with some impurity.[2] As the concentrations of chlorine atoms and the intermediate COCl are not known it is not possible to estimate the magnitude of the rate constants for the chain terminating processes nor for the chain continuing reactions by such studies. If, however, we take mixtures of carbon monoxide, hydrogen and chlorine and illuminate with light absorbed by the chlorine we may consider that the reactions resulting in the recombination of chlorine atoms (whatever they may be) are the same for both possible chains. The reactions in such a system may be formulated as follows

(1) $Cl_2 + h\nu = Cl + Cl^*$
(2) $Cl + H_2 = HCl + H$
(2a) $Cl + Cl_2 + CO = COCl + Cl_2$
(3) $H + Cl_2 = HCl + Cl$
(3a) $COCl + Cl_2 = COCl_2 + Cl$

with chain terminating processes such as

$$\left.\begin{aligned} COCl + Cl &= CO + Cl_2 \\ Cl + Cl &= Cl_2 \\ Cl + \text{wall} &= {}^1/_2Cl_2 \end{aligned}\right\} \quad (4)$$

the relative amounts of HCl and $COCl_2$ formed, in such a mixture will be determined by the rates

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[1] (a) Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B3**, 459 (1929); (b) Lenher and Rollefson, THIS JOURNAL, **52**, 500 (1930).

[2] Bodenstein and Unger, *Z. physik. Chem.*, **B11**, 253 (1931).