3. The errors found in the titration are caused by adsorption of iodide ions by the precipitate, and the error (adsorption) can be reduced to a very small value by titrating at 90°, or by digesting the precipitate at 90° in the presence of a slight excess of silver previous to finishing the titration at room temperature.

MINNEAPOLIS, MINN. RECEIVED MARCH 30, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Adsorption of Silver and Iodide Ions by Freshly Precipitated Silver Iodide. The Isoelectric Point of the Fresh Precipitate

BY I. M. KOLTHOFF AND J. J. LINGANE

In a previous communication,[1] we described the results of an investigation of the accuracy of the potentiometric iodide–silver titration. It was found that when the titration was performed at room temperature, to the equivalence potential, approximately 0.10% too much potassium iodide was required. In this paper we present experimental evidence which proves that the excess requirement of potassium iodide at room temperature is due to an adsorption of iodide ions by the fresh precipitate at the potentiometric end-point.

We have also directly determined the "isoelectric point" of freshly precipitated silver iodide. The isoelectric point, or "zero-point charge," is defined as the silver-ion concentration at which neither silver nor iodide ions are adsorbed by the precipitate.

In their study of the precision of the potentiometric iodide–silver titration, Lange and Berger[2] determined the adsorption of silver nitrate and potassium iodide on freshly precipitated silver iodide at various temperatures. They found that the adsorption of the "potential determining" silver and iodide ions agreed with the expression, $\Delta X = K \Delta \log C$; in which X is the amount adsorbed, K is a constant and C is the equilibrium concentration of the ion being adsorbed. They found that this relation was valid at temperatures between 30 and 90°. It is very doubtful, however, whether the values of X determined at the higher temperatures are really significant, because the fresh precipitate ages quite rapidly at higher temperatures, causing a continuous decrease in its adsorptive power with resultant continuous desorption of the ion initially adsorbed. We have found that this desorption process is very slow at room temperature in the presence of an excess of silver, but is greatly accelerated at the higher temperatures.

Lange and Berger concluded from their experiments that silver ions are adsorbed more strongly than iodide ions at equal equilibrium concentrations. Their conclusion was based on the erroneous assumption that neither adsorption of silver nor iodide ions occurs at the potentiometric end-point, or "equivalence potential," where $c\mathrm{Ag}^+$ in solution is equal to $c\mathrm{I}^-$. Actually, as will be shown in the present paper, the isoelectric point of freshly precipitated silver iodide at room temperature is found at a silver ion concentration of approximately 10^{-6} molar, the silver ion concentration thus being nearly 10,000 times as great as the iodide-ion concentration.

In agreement with Lange and Berger, Verwey and Kruyt[3] found in their work with well aged electrodialyzed silver iodide *sols* that the adsorption of iodide ions follows the expression $\Delta X = K \Delta \log C$. They could not determine the location of the isoelectric point directly without flocculating the sols, but with the aid of the foregoing expression they extrapolated to the point of zero adsorption (isoelectric point), and found that this point corresponded to a silver-ion concentration of 10^{-6} molar. This value agrees very well with the value we determined directly with a fresh *precipitate*.

Gorochovsky[4] found that the isoelectric point of silver iodide sols depended greatly on the silver iodide concentration of the sols. The results of his experimental work, however, are inconclusive since he did not correct for adsorbed silver or iodide ions on the surface of the silver iodide.

Lange and Berger mention the possibility of an

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[1] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1524 (1936).

[2] E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171, 980 (1930).

[3] E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, **A167**, 149 (1933).

[4] G. N. Gorochovsky, *J. Phys. Chem.*, **39**, 465 (1935); see also G. N. Gorochovsky and J. R. Protass, *Z. physik. Chem.*, **A174**, 122 (1935).

adsorption of silver ions from neutral solution on the glass walls of containing vessels, but they made no attempt to determine its extent. In order to exclude such possible adsorption we worked in dilute nitric acid medium.

Experimental

The materials and apparatus used in this work have already been described.[1] In all experiments the iodide solution was added at room temperature to a slight excess of silver solution, slightly acidified with nitric acid, and the same titration technique was followed as in the paper already referred to.[1]

In order to obtain quantitative information regarding the absorption of silver and iodide ions, it was necessary to know the relation between the measured e. m. f. of the titration cell and the silver-ion concentration of the solutions. As a result of many measurements of the e. m. f. obtained with solutions of known and widely varied silver-ion concentration, in which the total ionic strength and the concentration of nitric acid were the same as in the titrations, we found the following empirical relation: $E_{298} = 0.560 + 0.0591 \log (\mathrm{Ag^+})$. This equation holds at 25° for measurements in solutions 0.035 N in nitric acid, and 0.01 N in potassium nitrate, the potential of the silver iodide electrode being measured against the saturated calomel electrode with saturated potassium nitrate in the salt bridge.

The interpretation of the experimental data also required a knowledge of the solubility of silver iodide under the conditions of the titrations. We determined the solubility product by performing titrations with extremely dilute silver and iodide solutions, and calculated the desired quantity from the data so obtained.[5,6] The average value of the solubility product of silver iodide determined in this way was 2.18×10^{-16} at 25° in 0.035 N nitric acid ($\sqrt{S_{\mathrm{AgI}}} = 1.48 \times 10^{-8}$). Hence at the equivalence potential $p\mathrm{I} = p\mathrm{Ag} = 7.83$, and $E = +0.098$ v.

Adsorption of Iodide at the Equivalence Potential.—The amount of iodide adsorbed at the equivalence potential was first determined by measuring the amount of iodide desorbed when a fresh precipitate at the equivalence potential was aged by digestion at 90°.

It was found that such a fresh precipitate aged only very slowly at room temperature. For example, in a typical experiment the titration was stopped when the e. m. f. reached 0.113 v. and had remained steady at this value for an hour. The mixture was allowed to age overnight at room temperature with constant stirring, during which time the e. m. f. only decreased to 0.098 v.; in other words, the pAg only increased from 7.56 to 7.83. Therefore, only a very slight desorption of iodide takes place during the time required to reach steady e. m. f. at room temperature (*ca.* two hours), previous to digestion at 90°.

The amount of excess iodide retained by a fresh precipitate at room temperature at the equivalence potential was then determined in the following way. A titration was carried out according to the careful technique described in a previous paper,[1] using exactly known amounts of silver and potassium iodide. The titration was stopped when the e. m. f. reached +0.091 v. (practically the equivalence potential), and had remained steady at this value for an hour. A slight excess of pure solid potassium bicarbonate was added to neutralize free nitric acid, and thus eliminate the possibility of oxidation of desorbed iodide by the acid during the digestion. The mixture was then heated to 90–95°, and digested for twenty hours at this temperature under reflux. After cooling to room temperature, the mixture was again acidified to a concentration of 0.035 N in nitric acid, the e. m. f. was measured and found to be −0.075 v., corresponding to a change in pAg from 7.94 to 10.74, showing that much iodide was desorbed during the digestion. This desorbed iodide was titrated potentiometrically with 0.01 N silver nitrate, and found to correspond to 1.39 mg. of potassium iodide. 1.6241 g. of potassium iodide was used in the preparation of the silver iodide, hence the error due to adsorption of iodide amounts to 0.086%, whereas in the precise titrations[1] an error of 0.1 ± 0.02% was found. Within the experimental error, therefore, this deviation can be attributed to iodide adsorbed on the precipitate at the equivalence potential.

Although the precipitate was obtained by adding the iodide solution to the silver solution, the objection might be raised that the excess iodide in the precipitate at the equivalence potential is occluded within, and not adsorbed on, the precipitate. In the following manner it was shown that the excess iodide was actually absorbed. If iodide ions are primarily adsorbed by silver iodide, then either hydrogen or potassium ions (or both) must be adsorbed as counter ions, since these are the only cations present in the solution. The univalent counter ions may be replaced by a cation of higher valence. Thus, if a dilute solution of aluminum is added to the system, the following replacement reaction will take place

$$\mathrm{AgII^-}\left|\underset{\text{Counter ion}}{\mathrm{K^+}} + \underset{\text{Solution}}{1/3\mathrm{Al^{+++}}}\right. \longrightarrow \mathrm{AgII^-}\left|\underset{\text{Counter ion}}{1/3\mathrm{Al^{+++}}} + \underset{\text{Solution}}{\mathrm{K^+}}\right.$$

The aluminum exchange experiments were carried out in the following way. Two fresh silver iodide precipitates were prepared by precipitating 0.01 mole of silver with slightly less than the equivalent amount of potassium iodide at room temperature, in a final volume of about 140 cc. The first precipitate was adjusted to a pAg of 6.0 (isoelectric point) by adding 0.01 N potassium iodide solution, and after the e. m. f. had become steady at this point, the precipitate was washed eight to ten times by decantation with 1.0×10^{-6} N neutral silver nitrate solution. The precipitate was then suspended in 50 cc. of a solution that was 6.0×10^{-5} molar in aluminum nitrate and 1.0×10^{-6} N in silver nitrate (isoelectric solution), and the suspension was stirred mechanically at room temperature for thirty minutes. The amount of aluminum in the solution was just sufficient to displace the adsorbed potassium or hydrogen ions equivalent to 0.1% adsorbed iodide, if iodide was adsorbed on the precipitate. The supernatant solution was poured off and tests for aluminum ion were made on 10-cc. portions, using 1,2,5,8-hydroxyanthraquinone as reagent, according to the procedure given by Kolthoff.[7] A pure water blank, and the original aluminum

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(5) I. M. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928).

(6) I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

(7) I. M. Kolthoff, *Chem. Weekblad*, **24**, 544 (1927).

solution, were used for comparison. The supernatant solution gave virtually as strong a reaction for aluminum as the original solution, showing that no aluminum ions were adsorbed or exchanged by the fresh silver iodide at the isoelectric point. In other words, there was no iodide adsorbed on the isoelectric precipitate.

The second fresh precipitate was adjusted to a *p*Ag of 7.8 (equivalence point) by the addition of dilute potassium iodide solution, and after the e. m. f. had become steady, the precipitate was washed by decantation with eight to ten portions of pure water. The washed precipitate was stirred with 50 cc. of 6.0 × 10^{-6} molar (18 × 10^{-5} *N*) aluminum nitrate solution for thirty minutes as in the case of the first precipitate, and the supernatant solution was tested for aluminum ion as before. The tests showed that practically all the aluminum (more than 80%) had disappeared from the solution on shaking with the equivalence-point precipitate. The amount of exchange found at this point corresponds to the presence of 0.08–0.09% *adsorbed* iodide.

The desorption and the exchange adsorption experiments furnish conclusive confirmation of the fact that freshly precipitated silver iodide (at room temperature) contains between 0.08 and 0.10% excess iodide in the adsorbed state at the equivalence potential. Incidentally it may be mentioned that from the change of the hydrogen-ion concentration of the supernatant liquid in the exchange experiments, it was found that potassium and not hydrogen ions were the counter ions originally adsorbed with the iodide.

Isoelectric Point of Freshly Precipitated Silver Iodide.—The silver ion concentration corresponding to the isoelectric point of silver iodide was determined in the following way. A slight deficiency of a solution of potassium iodide was added at room temperature to a solution of silver nitrate slightly acidified with nitric acid. Dilute potassium iodide solution was added until the *p*Ag indicated in Table I was reached, after which the mixture was stirred at room temperature for two to three hours until the e. m. f. became practically constant. The mixture was digested overnight at 90 to 95° in a closed glass-stoppered flask, and then cooled to room temperature and the e. m. f. measured. The direction in which the e. m. f. (*p*Ag) changed on digestion indicated whether silver or iodide ions had been desorbed, and the magnitude of the change was a measure of the amount desorbed. By repeating the experiments at various silver-ion concentrations, it was possible to locate the point at which there was no change in the e. m. f. on digestion (no desorption) and this point was the isoelectric point of the precipitate.

In the experiments in which iodide was desorbed, the free nitric acid in the solution (0.035 *N*) was neutralized with a slight excess of pure potassium bicarbonate before digestion, in order to prevent oxidation of the iodide. The solution was again acidified, after it had been cooled to room temperature for the final e. m. f. measurement.

The amount of silver iodide was the same in all experiments (0.01 of a mole), and the final volume of solution was 135 to 145 cc.

The data of the desorption experiments are given in Table I. The last column of the table gives the amount of silver or iodide desorbed, expressed in micro-equivalents (10^{-6} equivalents) per 0.01 mole of silver iodide.

TABLE I

RESULTS OF DESORPTION EXPERIMENTS. ISOELECTRIC POINT OF SILVER IODIDE

0.01 mole of AgI in all experiments, in volume of 135 cc. to 145 cc.; 0.035 *N* in nitric acid.

	E, volts		*p*Ag		X Micro-equiv. desorbed per 0.01 mole of AgI
	Before digestion	After digestion	Before digestion	After digestion	
1	0.3285	0.3441	3.92	3.66	12.6 Ag^+
2	.2977	.3192	4.45	4.08	6.7 Ag^+
3	.2673	.3002	4.96	4.41	4.1 Ag^+
4	.2431	.2707	5.37	4.91	1.1 Ag^+
5	.2061	.2265	6.00	5.65	0.18 Ag^+
6	.1999	.171	6.12	6.60	.07 I^-
7	.1974	.172	6.15	6.58	.09 I^-
8	.1828	.077	6.40	8.19	(.05) I^-

The data of the experiments in which iodide was desorbed are less reliable quantitatively, than in the experiments in which silver was desorbed, because of difficulty in obtaining steady e. m. f. readings in the acid iodide solutions. For this reason we have not extended the experiments very far to the iodide side.

An inspection of the data shows that the isoelectric point lies at a *p*Ag of about 6.05. This result is in excellent agreement with the value found by Verwey and Kruyt, who worked with well aged electrodialyzed silver iodide *sols*.

Adsorption of Silver and Iodide Ions by Freshly Precipitated Silver Iodide.—Precision titrations of silver with iodide were carried out at room temperature as described in a previous paper,[1] and the amounts of silver and iodide ions adsorbed by the fresh precipitate were calculated by comparing the titration curve obtained in this way with the theoretical curve. The theoretical curve is based on the assumption that the precipitate has no adsorptive properties.

The data obtained in a typical titration are given in Table II, and plotted in Fig. 1. The differences between points on the abscissas of the theoretical and experimentally observed titration curves at equal values of the e. m. f. are a direct measure of the amount of silver or iodide ions adsorbed by the precipitate.

The following examples will illustrate the method used to calculate the theoretical curve, and the amounts of silver and iodide ions adsorbed at various points on the experimental curve.

The initial amounts of potassium iodide and silver taken for the experiment were 1.61901 and 1.05426 g., respectively. Since the theoretical KI:Ag ratio is 1.53889, the theoretical amount of silver required to precipitate 1.61901 g. of potassium iodide is 1.05206 g. Therefore, the total amount of excess silver distributed between the liquid and solid phases, at the zero point on the curve before any dilute potassium iodide solution was added, was 1.05426 − 1.05206 = 0.00220 g. in 750 cc. If we assume that this excess silver is entirely in the liquid phase (no adsorption), the silver-ion concentration of the solution should be $2.72 \times 10^{-5}N$. Hence $p\text{Ag}_{\text{calcd.}}$ is 4.57, and $E_{\text{calcd.}}$ is +0.290 volt (see Fig. 1). However, the observed e. m. f. at this point was 0.283 volt, corresponding to a silver-ion concentration of $2.04 \times 10^{-5}\,N$ ($p\text{Ag}_{\text{obsd.}} = 4.69$). The difference between the calculated and observed silver-ion concentrations is, therefore, 6.8×10^{-6} equiv. per liter, corresponding to 5.1×10^{-6} equiv. per 750 cc. (5.1 microequivalents) which is the amount of silver adsorbed (X_{Ag}).

The theoretical end-point of the titration, corresponding to the original excess of 0.00220 g. of silver, is 1.96 cc. of 0.0104 *N* potassium iodide. After the addition of 1.9 cc., the observed silver-ion concentration was greater than that calculated, the difference corresponding to an adsorption of 0.3 of a microequivalent of iodide. Upon addition of more than 1.96 cc. of dilute iodide solution, the calculated iodide-ion concentration is found from the difference between 1.96 cc. and the amount added. The difference between the calculated and observed iodide-ion concentrations (multiplied by 0.75) corresponds to the amount of iodide adsorbed, after allowance for the amount of silver in the solution ($p\text{Ag}_{\text{obsd.}}$). For example, after addition of 2.3 cc., the excess iodide in the system (actually in the precipitate) corresponded to 3.52 microequivalents per 750 cc. and the solution contained 0.25 microequivalents of silver. Therefore, $X_{\text{I}} = 3.52 + 0.25 = 3.77$ microequivalents.

By reference to Fig. 1, it will be observed that the experimental and theoretical curves intersect at $E = +0.215$ v., corresponding to a *p*Ag of 5.85, and hence there is no adsorption of silver or iodide ions at this point (isoelectric point). This value for the isoelectric point is in very good agreement with the value 6.05 determined in the desorption experiments. It must be clearly understood that the isoelectric point determined in this experiment and the method used to calculate the adsorption

TABLE II

DATA IN REGION OF EQUIVALENCE POINT IN TITRATION AT ROOM TEMPERATURE. ADSORPTION OF SILVER AND IODIDE

1.61901 g. of potassium iodide in 100 cc. of water added at room temperature to 500 cc. of solution containing 1.05426 g. of silver. Titration finished slowly at room temperature with 0.0104 *N* potassium iodide solution. Final volume 750 cc.; 0.035 *N* in nitric acid.

0.0104 *N* KI, cc.	Volts	*p*Ag, obsd.	*p*Ag, calcd.	X_{Ag} Micro-equiv. per 0.01 mole AgI	X_1 Micro-equiv. per 0.01 mole AgI
0	0.283	4.69	4.57	5.1	
0.5	.274	4.84	4.69	4.3	
1.0	.260	5.08	4.88	3.8	
1.5	.238	5.45	5.19	2.1	
1.7	.225	5.66	5.44	1.1	
1.9	.211	5.92	6.08		0.3
2.1	.195	6.18	9.95		2.0
2.3	.177	6.48	10.33		3.8
2.5	.156	6.84	10.54		5.7
2.6	.145	7.03	10.61		6.7
2.7	.133	7.23	10.67		7.7
2.8	.121	7.43	10.73		8.7
2.9	.107	7.67	10.78		9.8
3.0	.090	7.96	10.83		10.8
3.1	.071	8.28	10.86		11.8
3.2	.049	8.64	10.90		12.8
3.3	+.029	8.98	10.93		13.8
3.5	−.007	9.61	10.99		15.4
3.7	.032	10.02	11.04		16.4
4.0	.055	10.42	11.11		16.9

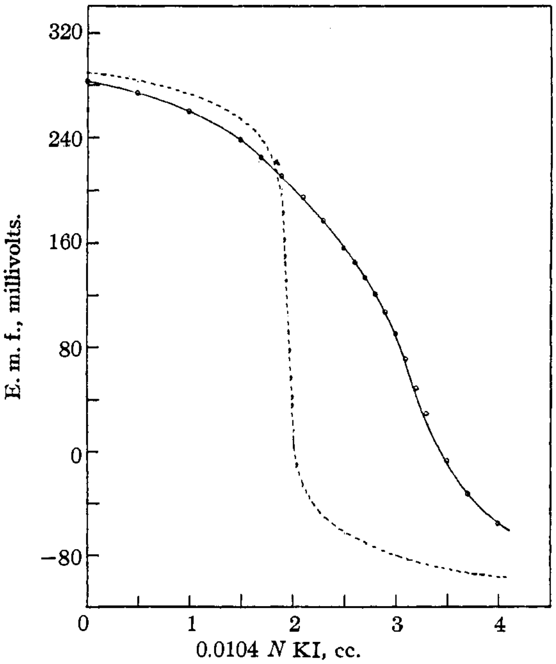


Fig. 1.—Titration curve at room temperature compared with theoretical (dotted) curve, data from Table II.

of silver and iodide ions by the precipitate, are entirely independent of any deductions or assumptions from the previous experiments. The calculations were based solely on the initial amounts of silver and potassium iodide taken and on the theoretical KI:Ag ratio.

Discussion

It is evident from Fig. 2, that the adsorption of silver ions by freshly precipitated silver iodide follows the expression $\Delta X = K\Delta \log C$. The same relation is found for the adsorption of iodide between pAg = 5.85 and pAg = 7.2, but at higher iodide-ion concentrations the values found for X_1 are less than correspond to the foregoing equation.

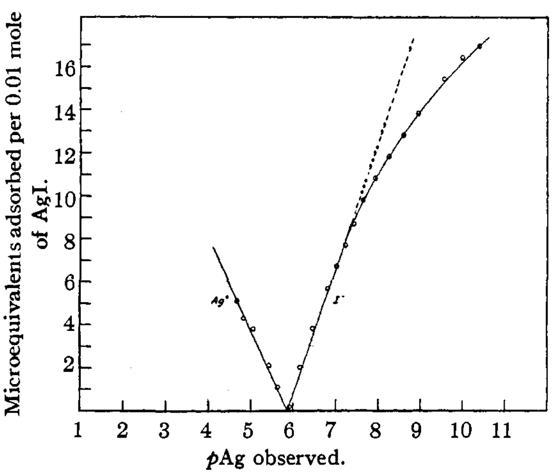


Fig. 2.—Adsorption of silver and iodide ions by freshly precipitated silver iodide, data from Table II.

It should be mentioned that this deviation is probably connected in some way with the fact that the e. m. f. measurements in the acid iodide solutions are somewhat unreliable. In addition, the precipitate ages more rapidly in the presence of excess iodide than when an excess of silver is present, and it is therefore to be expected that adsorption of iodide will become correspondingly less. It is possible, therefore, that the foregoing relation actually does hold over a wider range of iodide-ion concentrations, but it is very difficult to verify this possibility with a fresh precipitate. Working with an aged silver iodide *sol*, Verwey and Kruyt[3] found that the adsorption of iodide obeyed the foregoing relation over a much greater concentration range, than we have found with a fresh *precipitate*.

The K value found for iodide is greater than that of silver, indicating a greater adsorption of iodide than of silver ions. This result is contrary to that of Lange and Berger,[2] who failed to realize that over the region on their "silver adsorption" line between pAg 6.0 and 7.8, there is actually an adsorption of iodide and not of silver ions.

If the foregoing deductions from the experimental data are correct, the precipitate should have the stoichiometric composition at the isoelectric point (pAg = 6.0). As a matter of fact, we have found in the precise titrations that the theoretical KI:Ag ratio is found at the isoelectric point, when the proper correction is made for the excess silver in the solution. For example, in the titration whose data are given in Table II, if the end-point is assumed to be at the equivalence potential (+0.098 v.) the corresponding volume of 0.0104 N potassium iodide solution is 2.95 cc., the correction to the initial amount of potassium iodide taken is +5.1 mg., and hence the total amount of potassium iodide required to react with 1.05426 g. of silver is 1.6190 + 0.0051 = 1.6241 g. Therefore, the ratio KI:Ag calculated from these data is 1.5404, compared to the theoretical value 1.53889, and hence 0.10% too much potassium iodide was required. However, if the end-point of the titration is taken at the isoelectric point (E = 0.202 v., pAg = 6.05), the corresponding volume of 0.0104 N potassium iodide solution is 2.01 cc., the correction to the initial amount of potassium iodide taken is 3.46 mg., and hence the total amount of potassium iodide is 1.61901 + 0.00346 = 1.62247 g. The amount of silver corresponding to pAg = 6.05 in a volume of 750 cc. is 0.08 mg., and when this amount is subtracted from the initial weight of silver taken (1.05426 g.) the net amount of silver required is 1.05418 g. Therefore, the ratio KI:Ag is 1.62247 ÷ 1.05418 = 1.53908, which is only 0.006% larger than the theoretical ratio 1.53889. This result furnishes further striking confirmation of the deductions put forward in this paper.

Finally, this study shows that it is virtually impossible to obtain a true equivalent body of silver iodide by titration to the equivalence potential. Even if such a precipitate is washed repeatedly, it will be impossible to free it entirely of adsorbed iodide. A true equivalent body can be prepared by titration to the isolectric point (pAg = 6.0), but such a precipitate will remain a true equivalent body only as long as it is kept in the isoelectric solution (pAg = 6.0), because on washing with water it will again adsorb an excess of iodide.

Acknowledgment.—We wish to acknowledge our gratitude to the Graduate School of the University of Minnesota for the financial assistance which made this work possible.

Summary

1. The isoelectric point of freshly precipitated silver iodide has been found at a pAg of 6.0.

2. It has been shown that freshly precipitated silver iodide at the equivalence potential ($p\mathrm{Ag} = p\mathrm{I} = 7.83$) retains an excess of iodide adsorbed, corresponding to 0.09% of the total amount of iodide in the precipitate.

3. The adsorption of silver and iodide ions by the fresh precipitate follows the expression $\Delta X = K\Delta \log C$ in the pAg range between 4 and 7.2, iodide ions being more strongly adsorbed than silver ions.

4. The theoretical ratio KI:Ag is found in the potentiometric titration of silver with iodide at room temperature, if the end-point of the titration is taken at the isoelectric point ($p\mathrm{Ag} = 6.0$), instead of at the equivalence potential, and if a correction is applied for the excess silver ions in the solution.

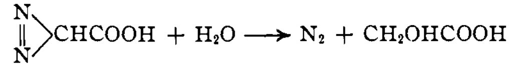
MINNEAPOLIS, MINN. RECEIVED MARCH 30, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Catalytic Decomposition of Diazoacetate Ion in Aqueous Solution[1]

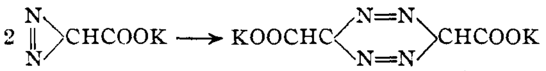
BY CECIL V. KING AND EDGAR DARE BOLINGER

Solutions containing salts of diazoacetic acid were first prepared by Curtius,[2] by alkaline hydrolysis of diazoacetic ethyl ester. The salts are, he found, stable in alkaline solution, but decompose with rapid evolution of nitrogen on neutralization with even carbonic acid, indicating that the acid is unstable



$$\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}\!\!>\mathrm{CHCOOH} + \mathrm{H_2O} \longrightarrow \mathrm{N_2} + \mathrm{CH_2OHCOOH}$$

Traube[3] made the sodium salt both by alkaline hydrolysis of the ester and by reduction of isonitroaminoacetic acid with sodium amalgam, and isolated the pure crystals from the solution. The preparation was further studied by Hantzsch and Lehmann[4] and by Müller,[5] who showed that the salts polymerize slowly in alkaline solution to the pseudo- or bi-diazoacetates



$$2\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}\!\!>\mathrm{CHCOOK} \longrightarrow \mathrm{KOOCHC}\begin{matrix}\diagup\mathrm{N{=}N}\diagdown\\ \diagdown\mathrm{N{=}N}\diagup\end{matrix}\mathrm{CHCOOK}$$

(or isomers)

Pure solid potassium diazoacetate is stable if kept dry, cool and in the dark. It explodes on heating or on shock.

In this research it was found possible to study the rate of nitrogen evolution when the potassium salt is dissolved in dilute alkali or in buffers of very weak acids and their salts. The reaction is exceedingly sensitive to general acid catalysis, and is of particular interest because the reaction of a negative ion with the acid catalyst is involved. So far as the authors are aware, no other case of this type has been studied. If it is assumed that the rate-controlling step in such a catalysis involves the transfer of a proton from the acid to the reacting molecule, a negative ion should be much more sensitive to such catalysis than a neutral molecule. In accordance with this supposition it is found that the hydrogen-ion catalysis of this reaction is greater than the corresponding diazoacetic ester catalysis by some ten million-fold.

The reaction is of interest, too, because it shows abnormalities of a type first observed in the basic catalysis of nitramide decomposition in m-cresol solution.[6] In that case catalysis by anion bases was found to vary inversely with the concentration of the corresponding acid so that it was necessary to extrapolate the molar basic constants to $1/C_{\mathrm{acid}} = 0$ to obtain comparable values. The catalysis by the anion of the solvent was variable and much lower than the value predicted from the catalysis by other bases. The latter abnormality was also found in the nitramide catalysis in water solution, *i. e.*, catalysis by the hydroxyl ion is lower than that predicted from the other

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[1] Condensed from Master's and Doctor's theses presented by Edgar Dare Bolinger in partial fulfilment of the requirements for these degrees at New York University, in 1934 and 1936.

[2] Curtius, *Ber.*, **18**, 1283 (1885).

[3] Traube, *ibid.*, **29**, 667 (1896).

[4] Hantzsch and Lehmann, *ibid.*, **34**, 2521 (1901).

[5] Müller, *ibid.*, **41**, 3136 (1908).

[6] Brönsted, Nicholson and Delbanco, *Z. physik. Chem.*, **A169**, 379 (1934).