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Velocity Coefficients of the Reaction between Ethyl Iodide and Silver Nitrate in Ethyl and Methyl Alcohol and Mixtures of These Solvents

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VELOCITY COEFFICIENTS OF THE REACTION BETWEEN ETHYL IODIDE
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AND MIXTURES OF THESE SOLVENTS.

BY J. N. PEARCE AND O. M. WEIGLE.

HISTORICAL.

The study of chemical reactions in various solvents is one that has been occupying the attention of chemists for a long time, for by this means it is thought that we may in time gain a closer insight into the mechanism of chemical reactions in general. A reaction frequently studied is that between alkyl halides and silver nitrate.

Burke and Donnan[1] made an extensive study of a number of reactions involving alkyl iodides and silver nitrate in ethyl alcohol. They found the reaction to be "pseudobimolecular" in character, i. e., the velocity coefficients of the simple bimolecular equation vary (increase) considerably with the initial concentration of the reacting substances, although it remains fairly constant during the course of any particular reaction.

They found also that the velocity coefficient, k, increases with increasing initial concentration of silver nitrate when the nitrate and the iodide are present in equivalent proportions. Using the same initial concentrations of silver nitrate and varying the proportions of ethyl iodide, the constants, k, are found to decrease with increasing concentration of ethyl iodide. When the iodide is kept constant, the velocity coefficients increase with increasing initial concentrations of silver nitrate. They were not able to explain the variation in the values of k.

The velocity coefficients in ethyl alcohol, using 0.025N, equivalent solutions of silver nitrate and alkyl iodides, were found to decrease in the following order: isopropyl, ethyl, n-propyl, methyl, n-butyl, isoamyl, isobutyl.

The velocity coefficients of the four iodides, methyl, ethyl, n-propyl, and n-butyl, were likewise determined in methyl alcohol, using 0.025N equivalents of iodide and silver nitrate.

In every case the velocity coefficients were greater in methyl than in ethyl alcohol, the ratio kMeOH$/k$EtOH being approximately equal to 2.

An addition of water to the extent of ten per cent produced only a slight increase in the value of k. The addition of benzene (10%), a non-dissociating solvent, gave a slightly lower value for k.

In a second paper, Burke and Donnan[1] give the results of further study of the reaction of ethyl iodide and silver nitrate in ethyl alcohol. Their purpose was to study the effect of the reaction products upon the velocity coefficients, and to determine which is the disturbing factor. Experiments proved that this disturbance is not due to ethyl nitrate, or ether, while nitric acid slightly retard the speed. The velocity coefficients are increased by the addition of both

[1]J. Chem. Soc. 85, 555 (1904).
[1]Z. physik. Chem., 69, 148 (1909).

Ca $(NO_3)_2$ and NH_4NO_3. A series of experiments on the amount and rate of formation of nitric acid during the reaction in ethyl alcohol showed that the nitric acid formed is always a constant percentage (about 70%) of the amount of silver nitrate which has reacted, and the amount formed is independent of the initial concentration of the reactants. More acid seems to be formed in mixtures of alcohol and water than in either pure solvent. The velocity coefficient curves for ethyl and methyl iodide in the aqueous alcoholic mixtures show a pronounced maximum near the alcohol end of the curve.

They offer as a tentative suggestion for the variation in the velocity coefficients with change in initial concentrations that "it is the undissociated silver nitrate which reacts and that the decrease in the bimolecular velocity coefficients which might be expected therefrom is compensated by the accelerating action of one of the reacting products." They were, however, unable to determine which of the products is the disturbing factor.

Donnan and Potts[1] made an attempt to determine whether the peculiar behavior already noted is due to the presence of the NO_3 group. They substituted silver lactate for silver nitrate in 60% alcohol-water solutions. Two series, using different equivalent concentrations of the reactants, were studied. The results showed that the disturbing factor in this case is absent. The ratio of the lactic acid formed to that of the silver lactate used up was the same as for nitric acid and silver nitrate, viz., approximately 70%.

Since free acid is one of the main products when solvents containing a hydroxyl group are used, they decided to carry out the experiments using ethyl iodide and silver nitrate in acetonitrile. No acid, other than a slight trace possibly due to impurities, was found. The experimental results resembled those obtained when alcohol was used as solvent. The simple bimolecular equation holds for all concentrations studied except 0.10 N, but the velocity coefficients vary with the initial concentrations of the reacting substances. This would show then that the variation is not dependent upon the formation of acid. Euler[1] studied the reaction between chlor-acetic acid and silver nitrate in water and in 45% alcohol-water mixtures. The reaction speed in 0.25 N equivalent solutions was decreased 100% in the presence of 0.5N nitric acid.

Senter[2] investigated the reactions between silver nitrate and bromacetic, α-brompropionic, α-brombutyric acids and their sodium salts. Traces of silver bromide added to the reacting mixtures were found to increase the initial velocity coefficients three to six times. The same was found to be true when traces of silver iodide were added to reaction mixtures of methyl iodide and silver nitrate in aqueous solutions. In these experiments the addition of nitric acid shows considerable retarding effect. Benzenesulphonic acid was found to have a still greater retarding effect than nitric.

Senter suggests the catalytic action of the silver halides as being the possible cause of the kinetic disturbances observed in reactions in alcoholic solvents.

No measurements of the velocity coefficients of the reaction in the mixed alcohols have been made and very little done with silver nitrate and ethyl iodide in methyl alcohol as solvent. It was thought some interesting facts might be brought to light through a systematic study of the reactions of silver nitrate

[1]J. Chem. Soc., 97, 1882 (1910).
[1]Ber. d. chem. Ges., 39, 2726 (1906).
[2]J. Chem. Soc., 97, 346 (1910).

and ethyl iodide in methyl alcohol, ethyl alcohol, and their binary mixtures.

With this idea in view, these reactions were carried out in the following alcoholic solutions:

> Ethyl alcohol—100%
> Ethyl alcohol— 75%, Methyl alcohol—25%
> Ethyl alcohol— 50%, Methyl alcohol—50%
> Ethyl alcohol— 25%, Methyl alcohol—75%
> Methyl alcohol—100%

MATERIALS AND SOLUTIONS.

Ethyl Alcohol. Ethyl alcohol, after standing for several months over two changes of fresh quicklime, was fractionated and kept over anhydrous copper sulphate until ready for use. It was then fractionated, refluxed with about 30 grams metallic calcium per liter for several hours, fractionated, and immediately refluxed with fused silver nitrate for two hours, and fractionated into dry glass stoppered bottles. A Glinsky distilling tube and soda lime or calcium chloride guard tubes were used. Alcohol thus prepared gave a conductivity of 2.4×10^{-7} at 25° C., measured by the Kohlrausch method, using bridge, induction coil, and telephone receiver. The Wheatstone bridge wire was calibrated by the method of Strouhal and Barns. The Arrhenius cell, as improved by Jones and Bingham, was used.

Methyl Alcohol. Kahlbaum's best grade of methyl alcohol was further purified in the same manner as the ethyl alcohol except that the copper sulphate treatment was omitted. The conductivity at 25° C. was found to be $.8 \times 10^{-6}$.

The mixtures of the alcohols were made up by weight, accurate to one-tenth gram per liter.

Silver Nitrate. Merck's chemically pure silver nitrate was twice recrystallized from a saturated solution in conductivity water by quickly cooling from 60° to 20°. The product was washed with conductivity water, filtered dry as possible on a Buchner funnel, dried in a Toluol bath at 109° C. for several hours, and cooled in a dessicator, the work being done either at night or in the dark. Several unsatisfactory methods were previously tried, but this gave a product of small dry crystals, showing no sign of coloring.

Ethyl Iodide. Kahlbaum's best grade of ethyl iodide was washed with dilute sodium hydroxide and water, dried over calcium chloride for two weeks, decanted, and fractionated. This, after nearly eleven months, has shown no tint of color.

Sodium Chloride. This salt was precipated by passing pure hydrogen chloride gas into a saturated solution of Merck's guaranteed chemically pure sodium chloride in conductivity water. The fine precipitate was filtered and washed on a Buchner funnel and dried in an electric oven at 110°. The portion used was heated, short of fusion, in a platinum crucible.

Ammonium Sulphocyanate. Kahlbaum's best grade of good clear crystals was used.

Nitric Acid. The best obtainable nitric acid, specific gravity 1.42, and free from chlorides, iodides and lower oxides of nitrogen, was kept in the dark in small bottles filled to the neck. Five cubic centimeters were used in each titration.

Iron Alum. Five cubic centimeters of a saturated solution, made from good clear crystals, were used in each titration.

Water. The water was purified by the method of Jones and Mackay[1]; ordinary distilled water was distilled from a large Jena flask containing a small amount of potassium bichromate and sulphuric acid. This was then doubly distilled from a similar flask and solution through a retort containing barium hydroxide and condensed through a block tin tubing. This water was used in making up all aqueous solutions.

Solutions. All solutions were made up to volume at 25° C. Alcoholic solutions of silver nitrate and ethyl iodide were prepared seven to twenty hours previous to using, and of such a strength that when equal volumes of the two were mixed the normality desired was obtained. 0.025N silver nitrate and ammonium sulphocyanate solutions were used in all titrations, the silver nitrate solution was made up by weight and checked against a standard sodium chloride solution by the Volhard method. The precipitate of silver chloride was filtered off before titrating with ammonium sulphocyanate. Since the results agreed very satisfactorily, the other solutions of silver nitrate were made up by weight.

APPARATUS AND METHOD.

In general the method used is similar to that followed by all experimenters in the measurement of velocity coefficients of chemical reactions.

All experiments were performed and solutions made up to volume in a constant temperature bath at 25°+.01. The motor driven stirrer kept the water in the large granite tank in constant motion. The heat was supplied by means of sixteen candle power electric light bulbs immersed in the bath and electrically controlled. The thermometer used was certified and graduated in tenths, such that it could easily be estimated to hundredths.

The bottles were suspended in the bath by means of a copper strip framework of clamps constructed for this purpose and which would accommodate twenty bottles at one time.

Every precaution was taken to keep the nitric acid, silver nitrate, ethyl iodide and solutions from the light. The reaction bottles and all solution bottles were thoroughly "seasoned," glass stoppered, and well protected by sacks of heavy black cloth or paper.

Equal volumes of each solution were quickly poured together, stoppered and shaken thoroughly. Then ten cubic centimeters of the mixture, removed by a certified pipette previously warmed in the bath, were introduced into each of several small dry bottles which had been brought to temperature by suspension in the bath. The approximate instant of mixing was taken as the initial time. At previously decided instants, a known amount—always an excess—of 0.025N ammonium sulphocyanate was quickly poured from an Erlenmeyer flask into the reacting solution to stop the reaction. This mixture was then poured back into the flask, the bottle rinsed three times with chlorine-free distilled water, diluting the solution to over one hundred cubic centimeters. Five cubic centimeters each of a saturated solution of iron alum and of nitric acid were then added and the excess of ammonium sulphocyanate determined by titrating with 0.025N silver nitrate. From this the amount of silver nitrate remaining in the solution at the instant of stopping the reaction was easily obtained.

[1]Am. Chem. J. *19*, 83 (1897).

One minute is the unit of time. The unit of volume is one cubic centimeter. The unit of concentration for silver nitrate is the amount of silver nitrate in one cubic centimeter of 0.025N solution, e. g., the concentration of ten cubic centimeters of an 0.05N silver nitrate solution is twenty. The concentration of ethyl iodide is expressed in equivalent terms. Unless otherwise stated, all data is the average of duplicate experiments made the same day.

EXPERIMENTAL.

Where the reacting substances are present in equivalent amounts, the velocity coefficients, k, are calculated according to the usual bimolecular reaction formula: $(K = \frac{1}{t} \cdot \frac{x}{A(A-x)})$

where $\times$ is the portion of the silver nitrate transformed in time t and A is taken as its initial concentration.

In the case of all non-equivalent solutions the following form of the bimolecular equation was used: $(K = \frac{1}{(A-F)+t} \cdot \ln\frac{B(A-x)}{A(B-x)}$

where the characters have the usual meaning.

Table I gives the results of duplicate experiments carried out in each of the five solvents, using equivalent solutions. For any particular reaction, the velocity coefficients show a fairly constant value. However, there is an unmistakable tendency to decrease, especially noticeable as the proportion of methyl alcohol increases, and this decrease is very much greater during the first part of the reaction. On the other hand, the velocity coefficients become larger as the proportion of methyl alcohol increases.

TABLE I.—VELOCITY COEFFICIENTS. 0.025N AgNO₃ AND 0.025N C₂H₅I
IN ALCOHOLS AS SOLVENTS.

100% Ethyl Alcohol			75% Ethyl Alcohol 25% Methyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	10.	---------	0	10.	---------	0	10.	---------
9	7.495	.00371	5	8.12	.00463	5	7.77	.00574
18	6.055	.00367	10	6.995	.00430	10	6.67	.00499
30	4.97	.00337	15	6.185	.00411	15	5.73	.00497
50	3.785	.00328	25	4.96	.00406	25	4.63	.00468
75	2.85	.00334	40	3.96	.00381	40	3.64	.00437
100	2.12	.00338	55	3.26	.00376	55	2.965	.00431
			75	2.69	.00362	75	2.33	.00438
			100	2.305	.00334	100	1.895	.00427

Note: c equals concentration of silver nitrate.

25% Ethyl Alcohol 75% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k
0	10.	---------	5	6.96	.00856
5	7.49	.00670	5	6.96	.00856
10	6.15	.00626	10	5.535	.00807
15	5.145	.00629	15	4.615	.00778
25	4.155	.00563	28	3.385	.00698
40	3.205	.00530	51	2.23	.00683
55	2.56	.00528	70	1.775	.00662
75	2.08	.00508			
100	1.62	.00517			

This is strikingly different from results obtained by Burke and Donnan (loc. cit.) with mixtures of ethyl alcohol and water in which they found a maximum near the alcohol end of the velocity coefficient—solvent curve. It is doubtful if one is justified in considering the mean values of these velocity coefficients, but they will be used to bring out more clearly some general relations.

A variation from the law of averages is shown by a slight sagging of the curve when the mean constants for any one series is plotted against solvents.

By plotting the coefficients for each solvent in a series against time as abscissae, it will be seen that curves for the mixed solvents are drawn towards that in pure ethyl alcohol, thus showing the dominating influence of the latter solvent.

Table II shows the results of a series of experiments similar to those of Table I except that non-equivalent solutions were used, and the same general relations apply here. A comparison of these tables shows that with the same initial concentration of silver nitrate, the velocity coefficients increase as the initial concentration of the ethyl iodide decreases.

TABLE II.—VELOCITY COEFFICIENTS. 0.025N AgNO₃ AND 0.0125N C₂H₅I
IN ALCOHOLS AS SOLVENTS.

100% Ethyl Alcohol			75% Ethyl Alcohol 25% Methyl Alcohol			50% Methyl Alcohol 50% Ethyl Alcohol		
t	c	k	t	c	k	t	c	k
0	10.	---------	0	10.	---------	0	10.	---------
10	8.445	.00407	5	8.90	.00528	5	8.78	.00598
21	7.29	.00443	10.5	8.145	.00492	10.5	8.07	.00521
36	6.875	.00337	15	7.70	.00473	15	7.43	.00566
55	6.045	.00386	20	7.32	.00456	20	7.055	.00540
75	5.71	.00371	26	6.94	.00447	26	6.645	.00541
130	5.285	.00343	33	6.65	.00425	33	6.235	.00542
200	5.06	.00374	40	6.295	.00444	40	6.10	.00510
			50	6.05	.00423	50	5.84	.00498

25% Ethyl Alcohol 75% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k
0	10.	---------			
5	8.46	.00804	0	10.	---------
10.5	7.59	.00728	5	8.345	.00884
15	7.03	.00732	10	7.355	.00891
20	6.63	.00710	18	6.51	.00853
26	6.30	.00681	25	6.075	.00831
33	6.005	.00666	32	5.82	.00792
40	5.83	.00628	35	5.70	.00802
50	5.615	.00607	43	5.495	.00797

A much greater difference may be observed in the values of the velocity coefficients in Tables II and III, than was just seen in a comparison of Tables I and II.

It will be noted that, other conditions being the same, a change in the initial concentration of the silver nitrate (Tables IV, VII, and VIII) produces a much greater change in the velocity coefficients than does a similar change in the initial concentration of the ethyl iodide (Tables IV, V, VI.)

A comparison of Tables VI and VIII, using the most concentrated solution of the silver nitrate with the weakest concentration of the ethyl iodide, and visa versa, shows that the reaction in the former proceeds much more rapidly than that in the latter, the same amount of silver nitrate being used up in one-third to one-fourth the time required by the corresponding reactions in Table VIII.

According to the law of mass action, the velocity of a bimolecular reaction should be directly proportional to the product of the reacting masses. That other influences than those due to concentration of the reacting substances are at work may be seen by a comparison of Tables VI and VIII. The values of k representing the proportionality between velocities and the products of the active masses vary widely for each solvent.

TABLE III.—VELOCITY COEFFICIENTS. 0.0125N AgNO₃ AND 0.0125N C₂H₅I IN ALCOHOLS AS SOLVENTS.

100% Ethyl Alcohol			75% Ethyl Alcohol 25% Methyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	5.	----------	0	5.	----------	0	5.	----------
11	4.06	.00421	10	4.46	.00242	10	4.205	.00378
21	5.82	.00294	23	3.88	.00251	22	3.675	.00328
45	5.25	.00245	31	3.61	.00248	31.1	3.30	.00331
70	2.735	.00237	45	3.26	.00257	45	2.85	.00335
110	2.06	.00260	65.5	2.81	.00238	65.5	2.39	.00333
135	1.695	.00290	85	2.53	.00229	85	2.14	.00315
170	1.55	.00262	110	2.20	.00251	110	1.835	.00314
			130	2.00	.00231	130	1.64	.00315

25% Ethyl Alcohol 75% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k
0	5.	----------	0	5.	----------
10	4.125	.00424	5	4.31	.00640
23	3.495	.00374	10	3.90	.00564
31	3.12	.00389	25	2.965	.00549
45	2.695	.00380	40	2.42	.00533
65.5	2.235	.00378	60	1.945	.00524
85	1.95	.00368	90	1.49	.00524
110	1.66	.00366	120	1.16	.00552
150	1.50	.00359			

TABLE IV.—VELOCITY COEFFICIENTS.   0.05N AgNO₃ AND 0.05N C₂H₅I.

100% Ethyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	20.	---------	0	20.	---------	0	20.	---------
9	9.29	.00540	4	12.725	.00812	4	10.56	.01163
25	4.72	.00558	7	9.41	.00804	8	7.625	.01014
50	3.375	.00493	10	8.085	.00737	12	5.975	.00978
70	2.485	.00505	15	6.49	.00694	18	4.56	.00941
95	1.995	.00475	21	5.285	.00663	20	4.41	.00884
			25	4.86	.00625	23	4.17	.00825
			40	3.63	.00564	30	3.435	.00804
			50	3.075	.00550	43	2.855	.00698

TABLE V.—VELOCITY COEFFICIENTS.   0.05N AgNO₃ AND 0.025N C₂H₅I.

100% Ethyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	20.	---------	0	20.	---------	0	20.	---------
10.75	13.13	.00689	5	14.33	.00991	7	12.21	.01452
20	11.585	.00648	7	13.485	.00943	10	11.38	.01417
39	10.51	.00598	10	12.505	.00915	13	10.92	.01370
55	10.17	.00618	13	11.80	.00913	16	10.645	.01319
			18	11.10	.00899	20	10.525	.01153
			26	10.555	.00866			

TABLE VI.—VELOCITY COEFFICIENTS.   0.05N AgNO₃ AND 0.0125N C₂H₅I.

100% Ethyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	20.	---------	0	20.	---------	0	20.	---------
5.04	17.695	.00355	2	18.18	.01190	2	17.60	.01754
12	16.335	.00621	4	17.25	.01084	4	16.445	.01743
24	15.555	.00541	6	16.56	.01084	6	15.915	.01633
30	15.31	.00553	8	16.17	.01033	8	15.595	.01567
36	15.175	.00570	10	15.83	.01041	10	15.36	.01578
			14	15.43	.01045	14	15.17	.01479

TABLE VII.—VELOCITY COEFFICIENTS.   0.025N AgNO₃ AND 0.05N C₂H₅I.

100% Ethyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	10.	---------	0	10.	---------	0	10.	---------
10.07	5.755	.00312	5	6.50	.00477	6.33	4.75	.00695
23	3.135	.00322	9	4.88	.00469	9	3.905	.00641
34	2.305	.00289	13	3.92	.00442	13.16	2.91	.00605
45	1.70	.00275	18	2.94	.00438	19	1.75	.00637
60	1.215	.00255	23	2.51	.00397	23.5	1.445	.00586
90.04	.585	.00245	30	1.905	.00380	28	1.17	.00558
100	.56	.00224	40	1.245	.00377	35	.93	.00506
			55	.765	.00355	45.5	.585	.00484

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TABLE VIII.—VELOCITY COEFFICIENTS. 0.0125N AgNO₃ AND 0.05N C₂H₅I.

100% Ethyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	5.	----------	0	5.	----------	0	5.	----------
4	4.05	.00270	4	3.92	.00313	4	3.57	.00438
7	3.64	.00235	7	3.395	.00289	8	2.645	.00426
10	3.14	.00254	10	2.795	.00310	13	1.85	.00422
17.14	2.34	.00240	17	1.975	.00300	16	1.505	.00420
28	1.585	.00229	23	1.52	.00290	20.5	1.20	.00396
35.5	1.26	.00220	30	1.09	.00290	24	.91	.00410
63	.42	.00235	37	.835	.00280	28	.78	.00386
			45	.59	.00280	32	.615	.00385

TABLE IX.—VELOCITY COEFFICIENTS. 0.0125N AgNO₃ AND 0.025N C₂H₅I.

100% Ethyl Alcohol			50% Ethyl Alcohol 50% Methyl Alcohol			100% Methyl Alcohol		
t	c	k	t	c	k	t	c	k
0	5.	----------	0	5.	----------	0	5.	----------
10	3.865	.00274	5	4.17	.00380	5	4.015	.00463
19.08	3.175	.00265	10.5	3.72	.00302	10	3.28	.00466
30	2.65	.00248	15	3.27	.00313	15	2.705	.00472
45	1.88	.00268	25	2.55	.00314	25	1.98	.00453
60	1.56	.00248	35	2.08	.00304	33	1.61	.00465
80	1.05	.00264	45	1.67	.00307	42	1.265	.00432
130	.425	.00285	60	1.30	.00295	51	.98	.00437
160	.225	.00306	80	.89	.00299	60	.77	.00440

In order to make certain that no changes were taking place in the apparatus solutions, or methods during the investigation, a check experiment was carried out with the results as shown in Table X. It is clearly seen that after nearly three months this data could be reproduced quite accurately.

TABLE X.—VELOCITY COEFFICIENTS. 0.025N AgNO₃ AND 0.025N C₂H₅I.

Average of two experiments January 15.			Solvent: Ethyl Alcohol A single experiment (Check) April 12.		
t	c	k	t	c	k
0	10.	------	0	10.	------
9	7.495	.00371	9	7.48	.00374
18	6.055	.00362	18	6.04	.00364
30	4.97	.00357	30	4.95	.00340
50	3.785	.00328	50	3.80	.00326
75	2.85	.00334	75	2.87	.00331
110	2.12	.00338	110	2.16	.00330

A tabulation of the mean velocity coefficients, Table XI, gives a general survey of the work covered, and may serve to bring out more clearly some of the points already noted. A natural order of tabulation readily shows the increase of the velocity coefficients with increasing initial concentration of silver nitrate. Taking any given concentration of ethyl iodide, e.g. 0.0125N, the change in the

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velocity coefficients is considerable. This change is greater as the methyl alcohol increases. Again, consider a series in which the concentration of silver nitrate is the same, e.g. 0.0125N. The mean constants decrease with increase in the initial concentration of ethyl iodde, but the change is much less than in the former case. These facts, already observed by Durke and Donnan (loc. cit.) in the use of ethyl alcohol as solvent, are now applicable to these reactions carried out in methyl alcohol and in their binary mixtures.

TABLE XI.—MEAN VELOCITY COEFFICIENTS OF THE REACTIONS BE-
TWEEN SILVER NITRATE AND ETHYL IODIDE IN ALCOHOLS.

Silver nitrate	Ethyl Iodide	C2H5OH	75 per cent. 25 per cent.	50 per cent. 50 per cent.	25 per cent. 75 per cent.	CH3OH
0.0125N	0.05N	0.00239	------------	0.00294	------------	0.00410
0.0125N	0.025N	0.00270	------------	0.00314	------------	0.00454
0.0125N	0.0125N	0.00286	0.00239	0.00380	0.00380	0.00557
0.025N	0.05N	0.00274	------------	0.00417	------------	0.00589
0.025N	0.025N	0.00345	0.00396	0.00471	0.00571	0.00747
0.025N	0.0125N	0.00380	0.09465	0.00540	0.00695	0.00836
0.05N	0.05N	0.00534	------------	0.00681	------------	0.00913
0.05N	0.025N	0.00638	------------	0.00921	------------	0.01342
0.05N	0.0125N	0.00589	------------	0.01080	------------	0.01625

SUMMARY.

The velocity coefficients of the reactions of thirty-three of the forty-five possible combinations of concentrations, using 0.05N, 0.025N, and 0.0125N solutions of silver nitrate and ethyl iodide in ethyl alcohol, methyl alcohol, and three of their primary binary mixtures, were obtained.

The velocity coefficients of any particular reaction, calculated by the usual bimolecular equation, show in most cases a fairly constant value. However, they show a decrease as the reaction proceeds and this decrease is more marked in the methyl alcohol and in the mixtures than in the pure ethyl alcohol as solvent.

Time-constant curves for any one concentration in the solvents used show a displacement toward the ethyl alcoholic solvent, thus indicating that this solvent has the greater influence on the reaction.

This is also shown by plotting the mean velocity coefficients against solvents. A slight sagging of the curve shows that the velocity coefficients for the mixtures are a trifle smaller than would be expected from the law of averages.

For the concentration considered, the coefficients are always greater in methyl alcohol than in ethyl alcohol as solvent.

For any given initial concentration of ethyl iodide in the solvents used, the bimolecular velocity coefficients increase as the initial concentration of the silver nitrate increases. For a given initial concentration of silver nitrate, they decrease as the initial concentration of the ethyl iodide increases, but the change in the coefficients is very much less in the latter case.

The difference in the effects of the two reacting constituents, which is apparently due to the presence of an excess or large amount of silver nitrate, increases as the proportion of methyl alcohol in the solvent increases.