

the transfer of two electrons from the inner to the outer shell in one or both of two adjacent atomic kernels, the group of 8 being preserved about each, with 2 jointly held electrons constituting the bond. This hypothesis is sufficient to explain the restricted region of the periodic system in which elements characterized by multiple bond formation occur. To meet requirements imposed by the facts relating to stability, reactivity and free rotation, the electrons of unsaturated octets are assumed to be held in equilibrium positions at greater distances from the nucleus than in the ordinary case, the transfer from the extended position to the usual ones liberating energy. No attractive force between electrons is assumed, and the electron arrangement is taken as cubic, (though subject to distortion).

Upon this basis a mechanism is provided for addition and condensation reactions. Interesting viewpoints are afforded in the study of conjugation, the structure and substitution reactions of benzene, and tautomeric shifts of double bonds. Formulas are illustrated and discussed which represent (more satisfactorily in several cases than other current theories do) many of the properties of chain hydrocarbons, the oxides of carbon, the carbonyl and carboxyl groups, nitrogen, oxygen, and the hydrides and oxygen containing ions of boron.

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THE SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM SULFATE AND OF SODIUM, SULFATE

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Raymond B. Stringfield, in discussing the sodium manganate process for the manufacture of potassium permanganate,¹ points out certain solubility effects which are interesting from both the practical and the theoretical standpoint. In the course of the process potassium permanganate is separated by crystallization from a mother liquor which contains, in addition to permanganate, a small percentage of free alkali and varying quantities of the sulfates, chlorides and carbonates of sodium and potassium. Stringfield says, "Various mixtures of chlorides, carbonates and sulfates are observed to repress the solubility of permanganate greatly, a mother liquor of 3.0% being common, and 1.0% not uncommon, against a normal solubility of potassium permanganate in pure water of 6.0 to 7.0%." These facts suggested an investigation of the solubility of potassium permanganate in solutions of these salts. Sackur and Taegener² have determined the solubility in solutions of potassium carbonate, potassium chloride and potassium hydroxide at several temperatures. Their results

¹ Stringfield, *Chem. Met. Eng.*, **22**, 1027 (1920).

² Sackur and Taegener, *Z. Elektrochem.*, **18**, 723 (1912).

at 25° are given in Table III because of their interest in this connection. The values in the case of potassium hydroxide were interpolated from their data. This paper presents data on the solubility of potassium permanganate in solutions of potassium sulfate and of sodium sulfate.

All determinations of solubility were made at 25°. The thermometer used was a standard instrument. Richards and Yngve have shown³ that a thermometer may be calibrated within a certain temperature range by determining the solubility of sodium sulfate decahydrate at the temperature in question, as read, and correcting to the true temperature at which that solubility is found. The mean of two closely agreeing determinations of the solubility of sodium sulfate decahydrate at 25° as read from this thermometer was 21.802%. The value found by Richards and Yngve, calculated to the same basis, is 21.750%. The error is +0.052%, corresponding to an error in temperature measurement of about +0.04°. The mean of two very careful determinations of the concentration of a solution of potassium permanganate saturated at 25° as read was 7.097%. Interpolation from the results of Baxter, Boylston and Hubbard⁴ gives the solubility at this temperature as 7.104%. This difference, -0.007%, corresponds to an error in temperature measurement of about -0.03°. From these experiments it was concluded that the temperature as measured was accurate within the limits of experimental error in the determinations. The thermostat was of the usual electrically heated and regulated type. The temperature varied at most 0.02° from the desired temperature; but in the great majority of runs the temperature control was better than this.

The potassium permanganate, potassium sulfate and sodium sulfate were all an imported product, "for analysis," purchased before the war. Tests showed that the permanganate was free from chloride sulfate and the heavy metals. No oxides of manganese could be detected on dissolving and diluting with conductivity water. Analysis of the sulfates by precipitating and weighing as barium sulfate gave results which agreed with the theoretical values within a few hundredths of 1%. Qualitative tests showed that chlorides and the heavy metals were absent. Flame tests showed that other alkali metals were absent in the sodium sulfate. There was a very slight trace of sodium in the potassium sulfate. The sodium oxalate used in standardizing permanganate solutions was also an imported product prepared especially for that purpose. The other chemicals used were from the ordinary laboratory supply. The hydrogen peroxide used was freed from a small quantity of sulfuric acid which was present by shaking with barium carbonate and filtering. Hydrochloric acid was redistilled to free it from a small amount of the same impurity. Conductivity water was prepared by redistillation; first from alkaline permanganate, then from dil. sulfuric acid, and care was taken to exclude dust and fumes from the laboratory. It was preserved in thoroughly steamed, seasoned bottles until used.

The method of the investigation followed that of Baxter, Boylston and Hubbard.⁴ Stock solutions of the sulfates, saturated at room temperature, were prepared; and solutions of the approximate concentrations desired for the different runs were prepared

³ Richards and Yngve, *THIS JOURNAL*, **40**, 164 (1918).

⁴ Baxter, Boylston and Hubbard, *ibid.*, **28**, 1336 (1906).

when wanted by diluting these. Two large test-tubes were prepared for each determination by cleaning, steaming out and drying in an oven. A quantity of potassium permanganate crystals was introduced in excess of that necessary for saturation of the solution, and of such size as would pass a 6-mesh screen; then the solution which had been prepared for the run was added, and finally the tubes were sealed before a blast lamp. When it was desired to secure saturation with reference to both permanganate and sulfate, an excess of crystals of each substance was introduced. One tube from each set of two was rotated for 2 hours or longer at 30° or above. This was found to produce supersaturation with reference to 25° in a few trial runs with sodium sulfate and potassium sulfate solutions of different concentrations. After this supersaturation the temperature of the bath was reduced to 25° and held at that temperature. The second tube of each set was then fastened on the rotating device and both were rotated for 6 to 8 hours. A few trials showed that equilibrium could be reached in 4 hours, starting with potassium sulfate solution in contact with permanganate crystals. A longer time was required in the case of sodium sulfate solutions; and the length of time necessary to reach equilibrium was greater the higher the concentration of sodium sulfate. In the runs whose results are given below, excellent agreement was always found between the analysis of the solution in which the equilibrium was approached from supersaturation and that of the solution in which it was approached from undersaturation. After the tubes had been rotated at 25° for 6 to 8 hours, they were fastened upright and allowed to remain in this position for 2 hours to permit complete settling. After breaking off the sealed ends of the tubes, portions for analysis were removed by means of pipets or siphon tubes and weighed in small-mouth conical weighing bottles. In somewhat more than half the runs portions were also transferred to pycnometers from each tube and the specific gravity was determined in the usual way. It was not always feasible to work with such large volumes of solution as were required for this.

Sulfates were determined by reducing potassium permanganate with sulfate-free hydrogen peroxide in the presence of a small quantity of hydrochloric acid, also sulfate-free, precipitating as barium sulfate, filtering on Gooch crucibles and igniting and weighing in the usual manner. Occlusion of manganous sulfate or even of sodium or potassium sulfate might occur in this process. The volume of solution at the time of precipitation was always large—about 600 to 700 cc. Occlusion should be lessened by keeping the volume large. A few trial runs in which different quantities of manganous salt were introduced by adding potassium permanganate to sulfate solutions and reducing and analyzing as above gave the correct values for the quantity of sulfate known to be present, within a few hundredths of 1%, in every case. About 20 precipitates from the regular determinations were treated to extract possible occluded manganous salts by fusing with sodium peroxide, adding water, acidifying and adding sulfurous acid to reduce any oxide of manganese which might be present. A few other precipitates were treated by boiling with nitric acid or aqua regia. The solutions were tested for the presence of manganese by heating a small portion with lead peroxide in nitric or sulfuric acid solution. In every case the test for manganese was negative. It is believed that error from occlusion was negligible.

Potassium permanganate was determined by adding an excess of stand-

ard ferrous sulfate solution in the presence of a small quantity of sulfuric acid and titrating back with standard permanganate solution. The

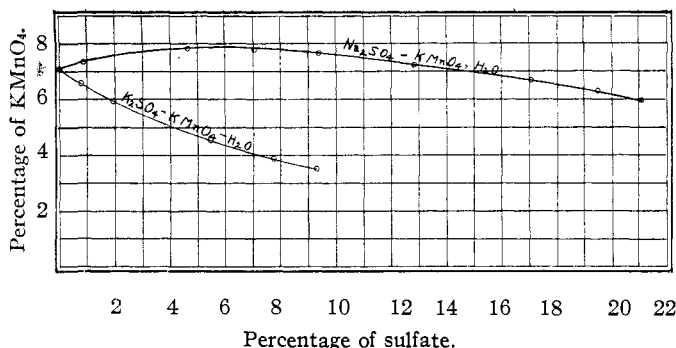


Fig. 1.—Solubility of KMnO_4 in solutions of K_2SO_4 and of Na_2SO_4 at 25° .

ultimate standard in this work was sodium oxalate of the highest purity. The data on these determinations are given in Tables I and II. They are also graphically represented in the curves of Fig. 1.

TABLE I

SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM SULFATE AT 25°

K_2SO_4 %	KMnO_4 %	Equivalents per liter $\frac{1}{2}\text{K}_2\text{SO}_4$	per liter KMnO_4	Parts per 100 parts solvent KMnO_4	Specific gravity $25^\circ/4^\circ$
0.00	7.10	...	0.469	7.64	1.0454
0.80	6.59	0.096	0.437	7.06	1.0483
1.98	5.92	0.239	0.395	6.29	1.0537 ^b
5.47	4.52	0.674	0.307	4.73	1.0730
7.79	3.87	0.972	0.266	4.02	1.0876
9.26 ^a	3.55	1.167	0.247	3.68	1.0979
10.75	0.00	1.340	1.0864

^a Saturated in the presence of K_2SO_4 and KMnO_4 crystals.

^b Calculated.

TABLE II

SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF SODIUM SULFATE AT 25°

Na_2SO_4 %	KMnO_4 %	Equivalents per liter Na_2SO_4	per liter KMnO_4	Parts per 100 parts solvent KMnO_4	Specific gravity $25^\circ/4^\circ$
0.00	7.10	...	0.469	7.64	1.0454
0.88	7.33	0.131	0.490	7.91	1.0554
4.62	7.83	8.50
7.05	7.75	1.107	0.548	8.40	1.1180
9.34	7.67	8.31
12.85	7.27	7.84
17.05	6.68	7.16
19.43	6.25	3.382	0.489	6.67	1.2363
21.04 ^a	5.91	6.28
21.80	0.00	3.705	1.2071

^a Saturated in the presence of KMnO_4 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals.

TABLE III
SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM CARBONATE,
CHLORIDE AND HYDROXIDE² AT 25°

Equivalents electrolyte per liter	Equivalents of $KMnO_4$ per liter in solutions of		
	K_2CO_3	KCl	KOH
0.1	0.4375	0.4315	...
0.5	0.306	...
1.0	0.2589	0.220	0.228 ^a
2.0	0.1432	0.153 ^a
4.0	0.093	0.102 ^a
6.0	0.092 ^a
8.0	0.046 ^a
10.0	0.032 ^a

^a Interpolated.

The weights and the volumetric apparatus used throughout all the work were calibrated and the necessary corrections were applied.

The specific gravities of sodium sulfate, potassium sulfate and potassium permanganate solutions of various concentrations were determined at 25°. The pycnometers used were of the Geissler type of 25 and 50 cc. capacity. Each pycnometer was repeatedly calibrated by determining the weight of conductivity water, recently boiled, which was held at 25°. Practically every solution whose specific gravity was determined was analyzed. In a few cases solutions were prepared by diluting weighed

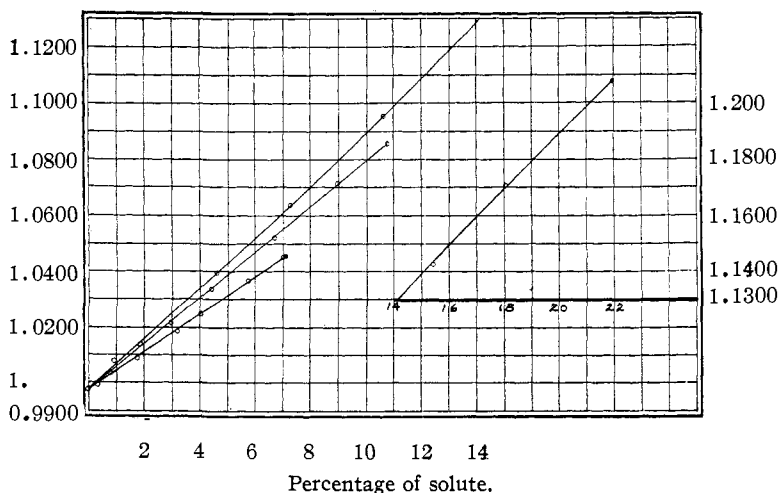


Fig. 2.—Specific gravities of solutions of Na_2SO_4 , K_2SO_4 and $KMnO_4$ at 25°/4°. The order of curves from left to right is Na_2SO_4 , K_2SO_4 , $KMnO_4$ and Na_2SO_4 .

quantities of solution of known concentration with known weights of water. The data are given in Tables IV, V and VI and are represented graphically by means of the curves of Fig. 2. All specific gravities are given in terms of that of water at 4° taken as unity.

TABLE IV
SPECIFIC GRAVITIES OF SODIUM SULFATE SOLUTIONS AT 25°/4°

Na ₂ SO ₄ %	<i>N</i>	Sp. gr.	Na ₂ SO ₄ %	<i>N</i>	Sp. gr.
0.88	0.125	1.0079	10.61	1.636	1.0952
1.77	0.252	1.0135	15.44	2.484	1.1425
4.61	0.668	1.0393	18.09	2.981	1.1705
7.28	1.090	1.0638	21.80	3.705	1.2071

TABLE V
SPECIFIC GRAVITIES OF POTASSIUM SULFATE SOLUTIONS AT 25°/4°

K ₂ SO ₄ %	<i>N</i>	Sp. gr.	K ₂ SO ₄ %	<i>N</i>	Sp. gr.
0.76	0.088	1.0033	6.71	0.810	1.0520
2.97	0.348	1.0212	8.97	1.103	1.0712
4.44	0.527	1.0335	10.75	1.340	1.0864

TABLE VI
SPECIFIC GRAVITIES OF POTASSIUM PERMANGANATE SOLUTIONS AT 25°/4°

KMnO ₄ %	<i>N</i>	Sp. gr.	KMnO ₄ %	<i>N</i>	Sp. gr.
0.30	0.019	0.9992	5.72	0.375	1.0368
1.77	0.113	1.0089	7.01	0.464	1.0451
3.20	0.206	1.0186	7.10	0.469	1.0454
4.05	0.263	1.0245

Normality is stated in the above tables in terms of $\frac{1}{2}$ Na₂SO₄, $\frac{1}{2}$ K₂SO₄ and KMnO₄, respectively.

W. C. Mc. Lewis⁵ points out that the specific gravities of aqueous solutions may be represented fairly closely by an expression of the form, $S = S_0 + ac + bc^2$, where S is the specific gravity of the solution, S_0 is the specific gravity of the solvent at the temperature of experiment, c is the concentration of the solute in any convenient units, and a and b are constants determined by experiment. That portion of the above expression, $ac + bc^2$, which gives the increase in specific gravity for the particular solution and concentration over the specific gravity of water, may be derived from the specific-gravity curve for the solution by subtracting the specific gravity of water from the specific gravity for a given concentration as read from the curve. If the law holds for solutions containing two or more salts, the specific gravities of such solutions should be given by the expression, $S = S_0 + (ac + bc^2)_1 + (ac + bc^2)_2 + \dots$, where the increases in specific gravity are given for each of the salts at their particular concentrations by $(ac + bc^2)_1$, $(ac + bc^2)_2$, etc. The different values here indicated were found and summed up in an attempt to supply the missing values for the specific gravities of the solutions tabulated in Tables I and II. The method gives good results in the solutions containing potassium sulfate and potassium permanganate, as will be seen from Table VII.

⁵ Lewis, "A System of Physical Chemistry," Longmans, Green and Co., 1920, vol. I, p. 210.

TABLE VII

COMPARISON OF CALCULATED AND ACTUAL VALUES FOR THE SPECIFIC GRAVITIES OF SOLUTIONS CONTAINING POTASSIUM SULFATE AND POTASSIUM PERMANGANATE

K ₂ SO ₄ %	KMnO ₄ %	Sp. gr.	
		Calc.	Found
0.80	6.59	1.0487	1.0485
1.98	5.92	1.0537
5.47	4.52	1.0728	1.0730
7.79	3.87	1.0873	1.0876
9.26	3.55	1.0972	1.0979

The value for the specific gravity of the solution containing 1.98% of potassium sulfate and 5.92% of potassium permanganate as calculated was inserted in Table I. The attempt to calculate the specific gravities of solutions containing potassium permanganate and sodium sulfate failed in those cases where specific gravities had been determined, the values turning out lower than those found by experiment. The difference between calculated and actual results becomes rapidly greater as the concentration of the solution increases. Since metathesis occurs in this case, resulting in the formation of new substances in unknown quantities, this failure was to be expected.

Finally, three determinations of the solubility of potassium permanganate in solutions containing known concentrations of sodium sulfate and potassium sulfate were made in an attempt to discover the specific effect upon the solubility of potassium permanganate in a solution of either sulfate produced by adding the other. The saturation of solutions was carried out as above, even a longer time being allowed for reaching equilibrium. The concentrations of potassium sulfate and of sodium sulfate in the original solutions being known, the final analysis was for the determination of the permanganate content only. From the data thus secured the concentrations of the constituents of the final solutions were calculated. It was assumed that the excess permanganate crystals did not appreciably adsorb the sulfates present. The data are given in Table VIII.

The values of the first line under "Specific Effects" were calculated as follows. If we take as solvent the solution of sodium sulfate which contains the relative proportions of salt and water given in Cols. 2 and 4 of Line 1, under "Constituents" we have a solution containing 6.24% of sodium sulfate. Plotting the values of Table II, Col. 5, against the corresponding concentrations of sodium sulfate in percentages of the solution chosen as solvent and reading from the curve, it is found that a solution of this concentration will dissolve 8.48 parts of potassium permanganate per hundred parts of solvent. Calculating again from Line 1 of Table VIII, it is found that when 5.00 parts per hundred of potassium sulfate are added to the solvent the solubility of permanganate is reduced to 5.33 parts per hundred, a

decrease of 3.15 parts per hundred. The other values were calculated in the same manner. Within the limits covered by these experiments, potassium sulfate acts powerfully to decrease the solubility of potassium permanganate in solutions of sodium sulfate. The effect of sodium sulfate in increasing the solubility in solutions of potassium sulfate is much smaller. The work had to be discontinued at this point, so that no further determinations in this series could be made.

TABLE VIII
SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM AND SODIUM SULFATES AT 25°

Constituents of Solutions			
K ₂ SO ₄ %	Na ₂ SO ₄ %	KMnO ₄ %	H ₂ O %
4.53	5.66	4.83	84.98
5.73	3.34	4.40	86.53
6.77	1.32	4.03	87.88

SPECIFIC EFFECTS ON SOLUBILITY OF POTASSIUM PERMANGANATE IN PARTS PER 100 PARTS OF THE SOLUTION CHOSEN AS SOLVENT

In Na ₂ SO ₄ Solution				
Na ₂ SO ₄ %	Normal solubility	K ₂ SO ₄ introduced	Solubility	Decrease
6.24	8.48	5.00	5.33	3.15
3.72	8.38	6.38	4.90	3.48
1.48	8.01	7.59	4.52	3.49
In K ₂ SO ₄ Solution				
K ₂ SO ₄ %	Normal solubility	Na ₂ SO ₄ introduced	Solubility	Increase
5.06	4.97	6.32	5.40	0.43
6.21	4.56	3.62	4.77	0.21
7.15	4.25	1.39	4.26	0.01

There is, as yet, no theory upon the basis of which the effect of one very soluble electrolyte upon the solubility of another of the same nature can be quantitatively predicted. Harkins⁶ shows that in the case of a uni-univalent salt of moderate solubility the solubility of the salt is reduced by the addition of an electrolyte which gives a common ion, the curves showing a regular decrease in solubility of the saturating salt as the concentration of the added salt increases. All the curves fall in a limited and well defined group. Curves for salts with a solubility in water up to about one equivalent per liter fall in this group,⁷ the curves falling higher and higher in the group as the solubility in pure water increases. The case of the solubility of potassium permanganate in any solution where a common ion is present comes under this rule, since its solubility in pure water at 25° is 0.469 equivalent per liter. When the curve for the solubility of

⁶ Harkins, THIS JOURNAL, 33, 1854 (1911).

⁷ Ref. 6, p. 1859.

potassium permanganate in solutions of potassium sulfate is plotted, using the same units which Harkins uses, it is found to lie in the upper part of the characteristic group. The curves representing the solubility of this salt in solutions of potassium carbonate, potassium chloride and potassium hydroxide fall quite close to that representing its solubility in solutions of potassium sulfate. All these solubility curves are such as would be expected from a qualitative application of the solubility product principle.

The form of the curve for the solubility of potassium permanganate in solutions of sodium sulfate is unusual. In general, the effect of an electrolyte which does not give a common ion is to increase the solubility of the saturating salt, as a result of metathesis, whatever the concentration of the added electrolyte. Here the effect in increasing the solubility rises to a maximum at about 6% of sodium sulfate as the concentration of this salt increases. At higher concentrations of sodium sulfate, however, the effect is just reversed. A like effect is found in some other cases. The curves for the solubility of calcium sulfate in solutions of magnesium chloride, of sodium chloride and of sodium nitrate, for example, pass through such a maximum. For the form of such curves there seems to be no satisfactory explanation.

The mother liquors from which potassium permanganate is crystallized contain very large percentages of sodium salts, but only small percentages of potassium salts other than the permanganate. Sodium carbonate and sodium chloride have solubilities in water of the same order of magnitude as that of sodium sulfate. Two of these three salts will practically always be present in the mother liquors; and all three may be present. The particular salts present and their concentrations will depend upon the procedure which is being followed. It is difficult to account for the low concentrations of permanganate in the mother liquors which Stringfield reports, unless some such effect as that which has been found here in connection with concentrated solutions of sodium sulfate is responsible.

Summary

This paper reports the results of a study of the solubility of potassium permanganate in solutions of potassium sulfate and of sodium sulfate at 25°, and gives data on the specific gravities of solutions of sodium sulfate, potassium sulfate and potassium permanganate at the same temperature. The solubility of potassium permanganate in solutions of potassium sulfate decreases with increasing concentration of sulfate. In solutions of sodium sulfate the solubility of this salt increases with increasing concentration to a maximum in solutions containing about 6% of sodium sulfate; then there is a slow decrease in solubility to a minimum in solutions which contain the maximum quantity of the salt which can go into solution in the presence of potassium permanganate crystals. For the lower concentrations of each

sulfate, potassium sulfate acts powerfully to decrease the solubility of potassium permanganate in solutions of sodium sulfate, while sodium sulfate increases its solubility in solutions of potassium sulfate to a much smaller degree.

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ADSORPTION OF IODINE BY SILVER IODIDE

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On page 98 of Bancroft's "Applied Colloid Chemistry,"¹ we find the following statement:

"Carey Lea² has shown that silver iodide adsorbs iodine strongly. This property of silver iodide was verified by shaking portions of freshly precipitated and still moist AgI with iodine solutions. An alcoholic solution of iodine, diluted until it has a pale sherry-wine color is quickly decolorized by AgI and the same thing happens with a very dilute solution of iodine in KI which in a few minutes becomes as colorless as water. It is probably this adsorption which makes silver iodide photographic emulsions apparently less sensitive than the silver bromide emulsions. If so, it should not be difficult to overcome this trouble."

Experiments were performed to determine whether adsorption did take place. Acetone, water-free methyl alcohol, 95% ethyl alcohol, and a water solution of potassium iodide were used as solvents for the iodine, which was purified several times by grinding with potassium iodide and then subliming. Standardized sodium thiosulfate solution (1 cc. = 0.0023 g. of iodine) was used for titration. Silver iodide was made by precipitating from solutions of potassium iodide and silver nitrate of strength ranging from *M* to 0.1 *M*. The potassium iodide and silver nitrate used were purified by recrystallization. All experiments were performed in a room with no actinic light present.

In the first series of experiments the precipitated silver iodide made from *M* solutions of silver nitrate and potassium iodide was thoroughly washed, dried and passed through a 100-mesh screen, in order to have fairly uniform particles. In each of these experiments 0.2 g. of dry, powdered silver iodide was added to 25 cc. of the solvent containing 0.05 g. of the purified iodine. The container was stoppered and the mixture shaken for 1 minute, 5, 10, 15, 20 and 30 minutes. Care was taken not to increase the temperature appreciably while shaking. The mixture was filtered rapidly by suction, and the filtrate titrated with sodium thiosulfate solution for free

¹ Bancroft, "Applied Colloid Chemistry," McGraw Hill Book Co., 1921.

² *Am. J. Sci.*, [3] 33, 492 (1887); See also Problem 54 of Bancroft's "Research Problems in Colloid Chemistry." Nat. Research Council Reprint No. 13, 1921.