0.01 and 0.1 M concentrations. Since iodic acid may be considered almost completely dissociated at 0.01 M, it is believed that -1.195 volts should be accepted for the present as the standard potential for the iodine–iodate reaction (A). It is estimated that the probable error of this last value is about 0.002 volt.

Free Energy and Heat of Formation of Iodate Ion.—From the standard electrode potential given by this research one may calculate the standard free energy change at 298.1°K. for the reaction

$$^1/_2I_2(s) + 3H_2O(l) = 5/2H_2(g) + H^+ + IO_3^-$$
$$\Delta F^\circ_{298.1} = -5 \times 23066 \times (-1.195) = 137{,}819 \text{ calories}$$

Gordon[16] has computed the entropy of water from spectroscopic data and with the heat of formation of water[17] and the entropies of hydrogen[18] and oxygen,[19] he calculates the free energy of formation of water

$$3H_2 + 3/2\,O_2 = 3H_2O(l) \quad \Delta F^\circ_{298.1} = -170.070 \text{ calories}$$

By subtraction of the last reaction from the preceding reaction one may calculate the free energy of formation of iodate ion.

$$^1/_2I_2(s) + 3/2\,O_2 + {}^1/_2H_2 = H^+ + IO_3^- \quad \Delta F^\circ_{298.1} = -32{,}251$$

The entropies of iodine[20] and of iodate ion[21] are known in addition to those of hydrogen and oxygen. The entropy change in this reaction is 76.20 cal./deg. and combination with the value for the free energy change gives for the heat of formation of iodate ion $\Delta H^\circ_{298.1} = -54{,}966$ calories. It is well to note that this value at 298.1°K. is in good accord with the value at 291°K. given in the summary by Bichowsky and Rossini.[22]

The authors wish to thank Professor W. M. Clark and Dr. E. G. Ball of the Physiological Chemistry Department of The Johns Hopkins University for helpful advice.

Summary

The electrode potentials of the iodine–iodate electrode reaction have been measured at several concentrations and its standard electrode potential evaluated

$$^1/_2I_2 + 3H_2O = IO_3^- + 6H^+ + 5E^- \quad E^\circ_{298.1} = -1.195 \text{ volts}$$

The free energy, entropy and heat of formation of iodate ion have been evaluated.

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[16] Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

[17] Rossini, *Bur. Standards J. Research*, **6**, 1 (1933).

[18] Giauque, THIS JOURNAL, **52**, 4831 (1930).

[19] Johnston and Walker, *ibid.*, **55**, 172 (1933).

[20] Giauque, *ibid.*, **53**, 513 (1931).

[21] Ahlberg and Latimer, *ibid.*, **56**, 858 (1934).

[22] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936.

BALTIMORE, MD. RECEIVED NOVEMBER 5, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Catalytic Decomposition of Hydrogen Peroxide by Aluminum Oxyiodide Hydrosols

BY ARTHUR W. THOMAS AND BENJAMIN COHEN

The catalytic decomposition of hydrogen peroxide by aluminum oxyiodide hydrosols[1] has been investigated for the first time for the purpose of studying the changes of the iodide ion concentration in these colloidal systems under various conditions.

This particular reaction was chosen for the following reasons: (1) It has been shown by several investigators that over a large range of iodide concentration, the decomposition of hydrogen peroxide in neutral solution is strictly proportional to the iodide ion concentration. (2) Hydrous aluminum oxide itself, and also in the presence of several potassium salts used in this study, had no appreciable catalytic effect upon hydrogen peroxide. (3) The decomposition of hydrogen peroxide by the sols was homogeneous and first order.

The pH values of the hydrosols were about 5.6 and increased to a maximum of $p\text{H} = 8$ upon the addition of certain potassium salts. In this range of pH, the steady state function for the iodide–iodine couple as investigated by Abel[2] and Liebhafsky[3] indicates that less than 1% of the total iodide present in our hydrosol systems will be removed to form iodine or tri-iodide ion. In

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[1] Perhaps a better name is "basic aluminum iodide" hydrosols. They are known also as "aluminum oxide" hydrosols with sorbed and contra iodide ions.

[2] Abel, *Z. physik. Chem.*, **136**, 161 (1928).

[3] Liebhafsky, THIS JOURNAL, **54**, 1792 (1932).

TABLE I

PREPARATION AND PROPERTIES OF THE SOLS

Sols	Temp. and time of preparation		Time of dialysis, days	I content[a]	Al content[a]	Ratio $\frac{Al}{I}$	pH	P. F.[b]
1	Boiling	12 hrs.	10	0.290	39.1	135	5.61	1.8
2	Boiling	7 hrs.	12	.137	15.3	112	5.63	2.2
3	Boiling	7 hrs.	18	.244	40.4	166	5.68	2.7
4	90°	7 hrs.	10	1.570	134.5	87	5.65	4.0
5[c]	25°	7 days	14	0.040	30.7	768	5.66	1.15
6	Boiling	7 hrs.	11	2.234	277.7	124	5.78	3.5
7[d]	Boiling	7 hrs.	0	13.22	321.2	24	4.86	..
8	Boiling	7 hrs.	10	1.025	136.1	132	5.75	3.0

[a] In milliequivalents per liter. [b] P. F. = "Promotion Factor," defined as the ratio of the observed velocity constant to the velocity constant calculated for a system where all the iodide is free or unbound. [c] Sol 5 was rather unstable and began to precipitate after standing three weeks. [d] Sol 7 was used for e. m. f. measurements only. Iodide ion activities of sols 6, 7 and 8 were 7.9, 54 and 3.6×10^{-4}, respectively.

this sense, the reaction was independent of the pH changes encountered in the present investigation.

Preparation of Hydrosols.—The hydrosols used in this investigation were prepared by the action of dilute hydriodic acid solutions upon aluminum amalgam in all details as previously described.[4] The description of these sols is given in Table I.

Other Materials Used.—Merck "Superoxol" was distilled under reduced pressure in a previously steamed "Pyrex" glass apparatus and stored in paraffined containers. The 0.1 N potassium salt solutions were prepared from suitable purified materials and they had the following pH values: iodide 7.01, nitrate 6.48, acetate 6.42, sulfate 6.12 and tartrate 6.66; the pH values of the acetate and tartrate are lower than those found in solutions of these "neutral" salts owing to deliberate addition of some acetic and tartaric acids, respectively.

Measurement of H^+ and I^- Activities.—Electrode measurements were made at 25 ± 0.05°. The hydrogen ion activity of the sols was measured by means of the quinhydrone electrode using a saturated potassium chloride calomel half cell as the additional element. The platinized platinum hydrogen gas electrode was used when the pH value was near 8.

Iodide ion activity measurements were made with silver–silver iodide electrodes made up according to Owen.[5] Electrodes made in this way are reported to be reproducible to ±0.05 mv.[5,6] and have been found reliable in very dilute solutions.[6] In this work, silver–silver iodide electrodes were indistinguishable in 0.1 N potassium iodide, the precision of the potentiometer system being ±0.1 mv. In undialyzed sols, duplicate electrodes agreed within ±0.2 mv., whereas in dialyzed sols they performed less satisfactorily with variations frequently as large as one millivolt. The technique of measurement was as follows: a constant volume of salt solution (2 cc.) was added to 20 cc. of sol, the mixture shaken and two silver–silver iodide electrodes, fitted in a rubber stopper, were immersed in the solution. The cell was allowed to equilibrate overnight at 25°; using a saturated potassium chloride calomel cell as the additional element, the e. m. f. of the cells was then measured at three-hour intervals until constant readings were obtained.

The normal electrode potential of the silver–silver iodide electrode was taken as $E^0 = 0.151$ volt, the average of three values reported in the literature.[5,7,8]

Method of Measurement of the Velocity of Decomposition of Hydrogen Peroxide.—Since in the present work, the greatest iodide content of the reaction system was two milliequivalents per liter, it was found possible to employ the titration method, determining the concentration of hydrogen peroxide during the course of the reaction by titration with potassium permanganate solution.

The procedure was usually as follows: a 100-cc. portion of hydrosol was pipetted into a previously steamed 200-cc. "Non-Sol" glass bottle. A measured volume of salt solution (usually 10 cc.) was added. The mixture was shaken and then kept overnight in a water thermostat at 25 ± 0.005° to ensure equilibrium. To start the reaction a measured volume of hydrogen peroxide solution was added to the mixture. At various time intervals, a 25-cc. portion of the reaction mixture was withdrawn and permitted to flow into a 250-cc. Erlenmeyer flask containing 125 cc. of an ice and sulfuric acid mixture.[9] The oxygen was expelled from the reaction system before withdrawing aliquots by gently shaking the bottle in the thermostat, then removing the bottle from the thermostat and shaking the mixture violently for about ten seconds. Except when the reaction was relatively slow, the time of sampling was recorded as the time when the pipet was half emptied. Titration with potassium permanganate followed immediately.[10]

In some of the measurements (sols 1, 2, 3 and 6) the procedure was slightly changed. After the reaction had been started, 25-cc. portions of the reaction mixture were transferred into separate 250-cc. wide-mouthed glass-stoppered "Pyrex" flasks which had been well steamed previously.

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(4) Thomas and Tai, THIS JOURNAL, **54**, 841 (1932).

(5) Owen, *ibid.*, **57**, 1526 (1935).

(6) Keston, *ibid.*, **57**, 1671 (1935).

(7) Pearce and Fortsch, *ibid.*, **45**, 2852 (1923).

(8) Gerke, *ibid.*, **44**, 1684 (1922).

(9) "Stopping" the reaction by the ice–sulfuric acid mixture was effective due to dilution and cooling. Considering the fact that in acid solution, hydrogen peroxide will oxidize I^- to I_2, the titer of hydrogen peroxide would decrease 1% in the most unfavorable cases were this reaction to go to completion.

(10) No correction was made for the iodine formed during the titration of hydrogen peroxide by potassium permanganate since the error involved was within the precision of the experiment.

At various time intervals an ice and sulfuric acid mixture was poured into the vessels and titrated immediately with permanganate.[10] Although the second method obviated the necessity of withdrawing the entire reaction mixture from the thermostat to expel the oxygen, the precision was practically unaltered.

The concentration of hydrogen peroxide at the beginning of the reaction was adjusted to 0.5 N in the case of systems having 1.5 or more milliequivalents per liter of iodide. In other cases an initial concentration of 0.3 N hydrogen peroxide was used.

Measurements upon a given hydrosol were completed as soon as possible in order to avoid errors arising from the changes which these hydrosols undergo upon aging even at room temperature. During a series of measurements the reaction mixture was kept in the dark.

The reaction followed the first order equation

$$K = \frac{2.303}{t} \log \frac{a}{(a - x)}$$

where a was taken as the number of cc. of potassium permanganate solution used in the first titration and $(a-x)$ the number of cc. of potassium permanganate used after the reaction had progressed t minutes.

The precision of this method may be seen from some representative experiments which follow:

Sol (8) In absence of salts

t, min.	Cc. $KMnO_4$	$K \times 10^3$
0	40.07	..
59.26	32.50	3.55
128.8	25.20	3.60
214.9	18.35	3.64
	Av.	3.59[a]

[a] A duplicate series of measurements yielded the average value of $K = 3.61 \times 10^{-3}$.

Sol (8) In presence of 0.0087 N potassium tartrate

t, min.	Cc. $KMnO_4$	$K \times 10^3$
0	38.81	..
188.0	30.64	1.26
352.6	24.95	1.25
578.2	18.99	1.24
	Av.	1.25

1.544×10^{-3} N KI in presence of 0.06 N K_2SO_4

t, min.	Cc. $KMnO_4$	$K \times 10^3$
0	39.85	..
75.5	33.87	2.12
166.6	27.93	2.13
225.8	24.54	2.15
290.0	21.49	2.14
336.4	19.54	2.12
	Av.	2.13

Experimental Results

Neutral Salt Effect upon Decomposition of Hydrogen Peroxide by Potassium Iodide.—Since aluminum oxyiodide sols in the presence of added electrolyte have velocity constants approaching a value for which the total iodide of the system is unbound, it was thought advisable to investigate the salt effect on H_2O_2–KI systems under conditions comparable with those existing in the work on sols.

Table II shows a list of values for unimolecular velocity constants of a 1.544×10^{-3} N potassium iodide solution in the presence of various salt concentrations.

TABLE II

THE DECOMPOSITION OF HYDROGEN PEROXIDE BY 1.544×10^{-3} N KI IN THE PRESENCE OF POTASSIUM SALTS

Salt concn. equiv./liter	$K \times 10^3$ in presence of Nitrate	Acetate	Sulfate	Tartrate
0	2.15	2.15	2.15	2.15
6.0×10^{-4}	2.16	2.18	2.15	2.14
6.0×10^{-3}	2.15	2.23	2.16	2.19
6.0×10^{-2}	2.17	2.21	2.13	2.19

It can be seen from Table II that the salt effect is less than 4% over the concentration range investigated. Walton[11] observed similar behavior for the cases of potassium nitrate and sulfate. The specific constant of 0.001544 N potassium iodide calculated from the data in Table II is 1.39 min.$^{-1}$ which is in good agreement with Walton's[11] value of 1.35 and with Liebhafsky's[2,12] value of 1.38.

The specific constant increased with dilution; however, when corrections were made for the decomposition of hydrogen peroxide by water, the specific constant remained practically unaltered.

Effect of Salts upon the Decomposition of Hydrogen Peroxide by Sols

Neither pure hydrous aluminum oxide nor an aluminum oxychloride hydrosol (0.254 equivalent of aluminum and 0.006 equivalent of chloride per liter) alone or in the presence of the potassium salts (used in this study) had any effect upon hydrogen peroxide.

Typical results for the effect of the added salts are furnished by sol 4 (Table III) and by sols 6 and 8 (Table IV, Figs. 1 and 2). Ten cc. of salt solution was added to 100 cc. of the sol. Then 5 cc. of hydrogen peroxide solution was added to start the reaction. In the case of sol 6, precipitates were produced upon the addition of 0.05 and 0.1 N sulfate and tartrate. Sol 8 showed precipitation upon the addition of 0.1 N acetate, and 0.01 (and higher) sulfate and tartrate. In all

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(11) Walton, *Z. physik. Chem.*, **47**, 185 (1904).

(12) Liebhafsky and Mohammad, THIS JOURNAL, **55**, 3977 (1933).

instances reported in this paper, however, these precipitates remained uniformly suspended during the measurements. In a few experiments, not cited herein, where the precipitates settled out, analogous results were obtained also. In a separate experiment, dry potassium sulfate was added to sol 6 to render it 0.1 N with respect to the sulfate which completely precipitated the micelles. After thirty minutes of shaking, the system was centrifuged and the clear supernatant liquid analyzed for iodide. The value of 2.208 milliequivalents per liter was found as compared to 2.234 in the original hydrosol. By a similar procedure the clear supernatant liquid obtained from sol 8 (rendered 8.7 × 10^{-3} normal with respect to sulfate) showed an iodide content of 1.011 milliequivalents per liter compared to 1.025 in the original sol.

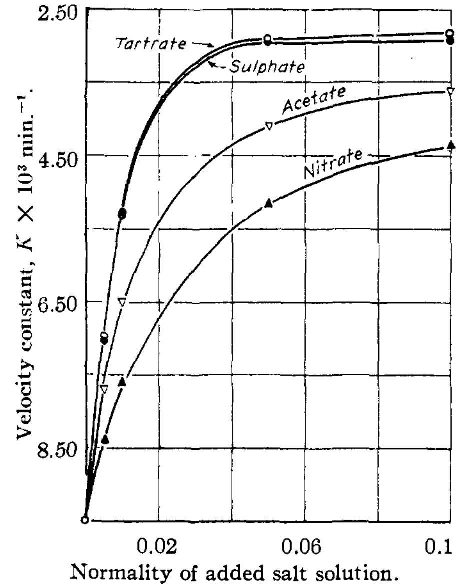

Fig. 1.—Effect of potassium salts on the velocity constant of sol 6. The velocity constant in the case of all iodide unbound is $K = 2.71 \times 10^{-3}$. The normality of salt in the system is found in this and in the remaining figures by dividing "Normality of Added Salt Solutions" by eleven.

TABLE III

EFFECT OF POTASSIUM SALTS ON VELOCITY CONSTANT[a] OF SOL 4

The velocity constant for the system with all the iodide unbound is 1.91 × 10^{-3} min.$^{-1}$.

Normality of added salt soln.	Nitrate	Acetate	Sulfate
0.0	7.74	7.74	7.74
.005	7.08	6.54	5.89
.01	5.50	4.89	3.19
.1	4.03	3.13	2.25

[a] Numbers represent 10^3 K min.$^{-1}$.

TABLE IV

EFFECT OF POTASSIUM SALTS ON VELOCITY CONSTANT[a] OF SOL 8

The velocity constant for the system in which the total iodide is unbound is 1.24 × 10^{-3} min.$^{-1}$.

Normality of added salt soln.	Nitrate	Acetate	Sulfate	Tartrate
0.0	3.59	3.59	3.59	3.59
.005	2.95	2.59	2.05	2.13
.01	2.66	2.23	1.38↓	1.40↓
.05	1.81[b]	1.56[b]	1.26↓	1.25↓
.1	1.60[b]	1.41↓	1.27↓	1.25↓

[a] Numbers represent 10^3 K min.$^{-1}$. [b] These sols became turbid upon addition of the electrolyte. ↓ Signifies precipitation.

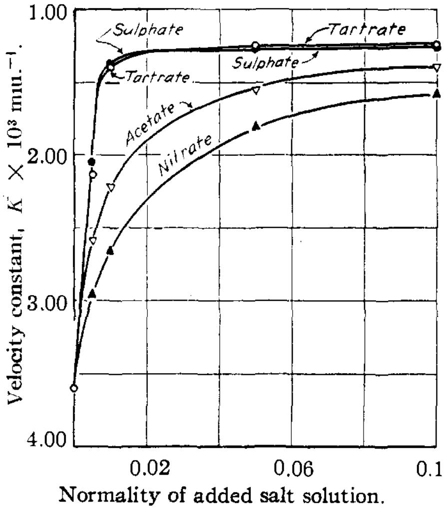

Fig. 2.—Effect of potassium salts on the velocity constant of sol 8.

Since added salts should displace bound iodide from the colloidal particles, it would appear from

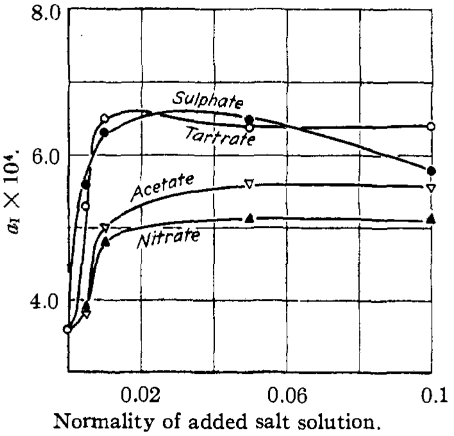

Fig. 3.—Effect of potassium salts on the iodide ion activity of sol 8.

the results of these experiments that the velocity constant for aluminum oxyiodide sols is a measure of the bound iodide of the system. To determine whether the iodide ion activity of the sol increased with addition of salts, silver–silver iodide electrodes were used upon sol 8 with salt concentrations similar to those used in the kinetic experiments. To 20 cc. of sol, 2 cc. of salt solution was added. pH measurements were also performed on identical systems. The results are plotted in Figs. 2 and 3.

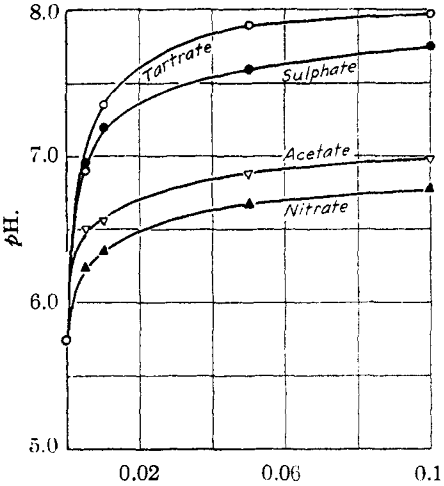

Fig. 4.—Effect of potassium salts on the pH of sol 8.

The iodide ion activity measurements were repeated upon sol 7 which was much richer in iodide than sol 8 and not dialyzed. The data obtained are plotted in Fig. 5.

The results obtained with the silver–silver iodide electrode indicate that iodide is being displaced from the colloidal micelles upon the addition of salts. However, it is not possible to estimate the iodide ion concentration in these systems, since the activity coefficients are unknown. The decrease in iodide ion activity at relatively high concentrations for some salts may be due to the decrease in the activity coefficient being larger than the amount of iodide that is displaced. Qualitatively the electrode measurements indicate that the order of effectiveness for potassium salts in increasing the iodide ion activity is about the same as that for decreasing the catalytic activity of these sols. The order of effectiveness of anions in increasing the pH of the sols is also the same.

According to the literature concerning the few iodide complexes[13] investigated, the catalytic effect on hydrogen peroxide for these complexes has been less than that for the iodide ion. This research suggests the further investigation of the catalytic effect of iodide complexes.

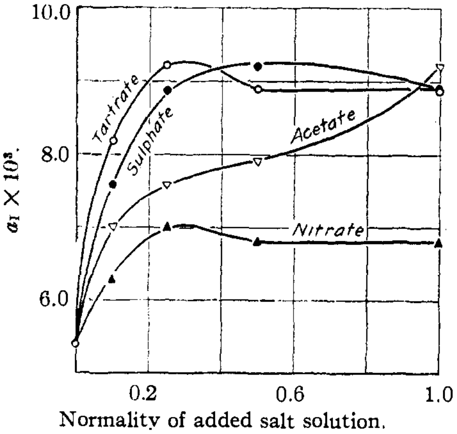

Fig. 5.—Effect of potassium salts on the iodide ion activity of sol 7.

Summary

The catalytic effect of aluminum oxyiodide hydrosols upon the decomposition of hydrogen peroxide is several times greater than that of aqueous solutions of iodide ions of the same concentration: this catalytic activity of these hydrosols is lowered by the addition of certain potassium salts, the order of effectiveness being tartrate > sulfate > acetate > nitrate, this being also the order for their effectiveness in increasing the iodide ion activity of the hydrosols.

It is apparent that basic aluminum micelles containing bound iodide (iodo groups) are more reactive toward hydrogen peroxide than iodide ion and it is postulated that the added anions displace iodo groups from the micelle, converting them to free iodide ions. Iodide ion activity measurements support this postulate and the order of effectiveness is identical to the effectiveness of these anions in replacing hydroxo groups from the micelle, converting them to hydroxyl ions.

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(13) Walton, *Z. physik. Chem.*, **47**, 185 (1904); Gooding and Walton, *J. Phys. Chem.*, **35**, 3612 (1931).