0.6255 gram substance in 11.90 grams naphthalene caused a depression of 0.685° in the freezing point of the solvent.

Calculated for $C_{42}H_{34}O_5$: Mol. wt., 618.3. Found: 530.

This ether appears to be somewhat more readily hydrolyzed to the carbinol than the ethers previously described. But even so, it is not affected by water and only very slowly by dilute alkalies.

The facts presented above were withheld until now from publication in THIS JOURNAL, in the hope that the synthesis of the much disputed *p*-hydroxy-triphenyl-methyl oxide would also be realized.[1] The appearance, however, of the paper by Schlenk in the last number of Liebig's *Annalen*[2] makes it desirable that the results obtained in this laboratory thus far be published now. Schlenk, too, attempted to prepare triphenylmethyl oxide by the use of various reactions. His results proved entirely negativ, and he concluded that this oxide is in all likelihood incapable of existence.

We have recently worked out a still different method for the preparation of triarylmethyl oxides. When triphenylmethyl carbonate (m. p. 205–10°) is heated under definit conditions it loses carbon dioxide and yields almost quantitatively triphenylmethyl oxide. The details of this reaction and the work relative to the oxides described by Werner,[3] Decker,[4] and by Barbier[5] will be given in a subsequent paper.

In connection with the oxides the study of the triarylmethylsulfides has also been in progress. Here, apparently, lead sulfide promises to give the best results.

ANN ARBOR, MICHIGAN.

STUDIES ON ENZYME ACTION. III. THE ACTION OF MANGANOUS SULFATE ON CASTOR BEAN LIPASE.

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In the first paper[6] of this series an experiment was described in which it was shown that the continued passage of an electric current through a suspension in water of the castor bean lipase preparation resulted in the production of a lipolytically active substance at the anode. As stated there, this substance was probably formed by some oxidation reaction of the preparation. Hoyer[7] found that small amounts of man-

[1] See footnote on title page of this paper.

[2] *Ann.*, **394**, 178 (1912).

[3] *Ber.*, 34, 3305 (1901).

[4] *J. prakt. Chem.*, **84**, 232 (1911).

[5] *Ann. chim.*, [5] **7**, 507 (1876).

[6] THIS JOURNAL, **34**, 735 (1912).

[7] *Z. physiol. Chem.*, **50**, 414 (1907). Cf. also Tanaka, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 11, 37 (1912).

ganous sulfate increased the activity of lipase to a greater extent than any other salt studied by him. In view of these facts, it appears reasonable to suggest the hypothesis that the activating action of manganous sulfate is based upon the property of the manganous salt of acting as an "oxygen carrier"[1] and in this way causing the production of a lipolytically active substance from the castor bean preparation by an oxidation reaction which would not take place (or only very slowly) in its absence. This hypothesis was tested in a series of experiments to be described in this paper.

Experimental.

The experiments may be divided into four groups, namely:

(1) Those in which the activity of the lipase preparation was tested after varying preliminary treatment, which consisted either in letting the mixture stand, or in passing air through the mixture in water, in the presence and absence of manganous sulfate, or in extracting and testing the filtrate and residue.

(2) A similar set of experiments with a lipase preparation which had been rendered lipolytically inactive by heat.

(3) A set of experiments similar to (1) and (2) but titrated by the formol method.

(4) Two comparative experiments (with and without heating) with somewhat larger amounts of lipase preparation and manganous sulfate.

The lipase preparation was obtained from castor beans, oil-free and finely ground as described in the former article. It was there found on testing with different esters, that the action on methyl acetate was not varied much by external influences, but that with ethyl butyrate, differences in action were observed which depended upon the conditions of the experiments and that at the same time sufficient action was obtained for purposes of comparison under the different conditions. Ethyl butyrate was, therefore, used to test the activity of the preparations in the experiments which follow. In every test, 1 cc. ester was used and the lipolytic activity determined at 38° for the lengths of time indicated in the tables. The acid formed was determined by titrating with 0.1114 *N* sodium hydroxide solution, using 5 drops of a 1% solution of phenolphthalein in 95% alcohol as indicator; the results of the action are given, in every case, in cc. of the sodium hydroxide solution.

Table I contains the results for the experiments in which the lipase preparation was used without preliminary heating in solution. These results as well as those in the other tables are each based upon two or more duplicate determinations not reported separately. Column 1 shows the number of the experiment, column 2, the weight of lipase preparation used, and columns 3, 4 and 5, the treatment preliminary to testing the

[1] Engler and Weissberg, "Vorgänge der Autoxidation," 1904, p. 111.

activity. The preparation was made up with 25 cc. water and $^1/_2$ to 1 cc. toluene, and tested directly, experiment 1, tested directly after addition of manganous sulfate (shown in column 5), experiment 4, or allowed to stand stoppered a certain number of hours before being tested (shown in column 3) or a slow current of air was passed first through a flask containing toluene and then through the solutions for the lengths of time indicated (column 4), experiment 3. If more than one of these treatments was applied, the Roman numerals preceding the numbers in the column show their order; thus in experiment 6, manganous sulfate was added and the solutions allowed to stand for 48 hours before testing their activity; in experiment 8, they were allowed to stand for 17 hours and air was passed through for 8 hours after manganous sulfate had been added, before the activity was tested; in experiment 5, manganous sulfate was added just before the activity test, the solutions having stood and air having been passed through for the lengths of time indicated.

TABLE I.—THE ACTION OF CASTOR BEAN LIPASE ON ETHYL BUTYRATE.

Expt. No.	Wt. of lipase. Gram.	Time of standing. Hours.	Time of action of air. Hours.	Wt. of $MnSO_4.4H_2O$ added. Milligrams.	Activity tested. Time of action. Hours.	Cc. 0.1114 N NaOH used. Lipase ester water.	Ester water.	Lipase water.	Action lipase ester.	
1[1]	0.2	..	..	...	50	2.50	0.20	0.70	1.60	
2	0.2	..	..	...	45	2.46	0.09	0.69	1.68	
3	0.2	..	18	...	45	1.80	0.11	0.50	1.19	
4	0.2	..	..	20	45	2.60	0.11	0.65	1.84	
5	0.2	16	4	II 20	45	1.95	0.11	0.74	1.10	
6	0.2	48	..	I 20	48	2.41	0.17	0.76	1.58	
7	0.2	16	4	I 20	45	2.50	0.11	0.75	1.64	
8	0.2	17	8	I 50	43	2.45	0.13	0.90	1.42	
9	0.2	..	..	50	43	1.20	0.13	0.78	0.29	Cold extraction, filtrate.
10	0.2	17	8	...	43	0.48	0.10	0.43	—0.05	
11	0.2	17	8	I 50	43	0.75	0.13	0.70	—0.08	
12	0.2	..	..	...	43	1.25	0.10	0.55	0.60	Cold extraction, residue.
13	0.2	..	..	50	43	1.68	0.13	0.85	0.70	
14	0.2	17	8	...	43	1.25	0.10	0.70	0.45	
15	0.2	17	8	I 50	43	1.68	0.13	0.70	0.85	

Column 6 shows the time of action at 38° in testing the activity, and columns 7–10, the results obtained in titrating after the action had proceeded the requisit time. Column 7 shows the amount of acid formed from the lipase preparation-ester-water mixture; column 8, that from the ester-water blank; column 9, that from the lipase preparation-water blank; and column 10, the amount of acid due to the lipase preparation-ester mixture, *i. e.*, [column 7 — (column 8 + column 9)]. The lipase

[1] This experiment is taken from the first paper.

preparation was treated in the same way preliminary to the activity test in the tests in which ethyl butyrate was subsequently added and in those in which it was not.

For experiments 9–15, the lipase preparation was ground with water, filtered through coarse filter paper, and the clear, yellow filtrate diluted so that 25 cc. portions corresponded to 0.2 gram of the original perparation. These were used for experiments 9–11. The residue after filtration was dried on a porous plate and 0.2 gram portions used for each of the experiments 12–15.

Experiments 1–8 show that the activity of the lipase preparation is decreased after standing in solution, but that if manganous sulfate is present the activity after standing or passing air through the solutions, while not as a rule greater than when tested immediately, tended to approach the value in magnitude. Experiments 9–11 show that the slight activity found in the filtrate from the preparation after extraction with water, disappeared on standing, even when manganous sulfate was present, while experiments 12–15 show that the residue contained material which was lipolytically active, and that increased activity was shown after the action of manganous sulfate.

In Table II the results obtained by testing the lipase preparation after it had been inactivated by heat and then subjected to varying treatment are given. Requisit portions of the substance were heated with 25 cc.

TABLE II.—THE ACTION OF CASTOR BEAN LIPASE ON ETHYL BUTYRATE AFTER HEATING.

Expt. No.	Wt. of lipase. Gram.	Time of standing. Hours.	Time of action of air. Hours.	Wt. of $MnSO_4 \cdot 4H_2O$ added. Milligrams.	Activity tested. Time of action. Hours.	Cc. 0.1114 *N* NaOH used. Lipase ester water.	Ester water.	Lipase water.	Action lipase ester.	
16.....	0.2	..	..	...	22	0.45	0.08	0.38	—0.01	
17.....	0.2	34	18	...	41	0.39	0.08	0.39	—0.08	
18.....	0.2	16	4	II 20	45	0.85	0.11	0.60	0.14	
19.....	0.2	18	..	I 20	45	0.75	0.11	0.61	0.03	
20.....	0.2	32	15	I 10	22	0.75	0.08	0.63	0.04	
21.....	0.2	34	18	I 50	41	1.32	0.21	0.80	0.31	
22.....	0.5	20	..	...	46	1.03	0.08	0.93	0.02	
23.....	0.5	..	20	...	47	1.00	0.08	0.89	0.03	
24.....	0.5	18	..	II 20	45	1.45	0.20	1.03	0.22	
25.....	0.5	..	20	II 20	47	1.25	0.10	1.08	0.07	
26.....	0.5	18	4	I 20	45	1.60	0.20	1.10	0.30	
27.....	0.5	..	20	I 20	46	1.32	0.13	1.07	0.12	
28.....	0.2	29	..	...	40	0.23	0.18	0.18	—0.03	Hot extraction, residue.
29.....	0.2	49	49	...	46	0.23	0.10	0.25	—0.12	
30.....	0.2	29	..	I 20	40	0.19	0.14	0.20	—0.15	
31.....	0.2	49	49	I 20	46	0.93	0.15	0.38	0.40	

water in test tubes, in a boiling water-bath, for two hours. The mixtures were then transferred to small flasks, the amount of water being increased to 40–50 cc. during the transfer, $^1/_2$–1 cc. toluene added and then the portions treated as indicated in the tables. The various columns in Table II have the same significance as in Table I.

The results of experiments 16–21 with 0.2 gram lipase preparation show that if no manganous sulfate is present, no activity is observed, but that if manganous sulfate is added, a distinct lipolytic action is apparent. With experiments 22–27, using 0.5 gram of the lipase preparation, there is apparently a very slight activity shown if no manganous sulfate is present, but much more marked activity if it is present. In experiments 28–31, the lipase preparation was boiled for an hour with water, filtered, the residue dried on a porous plate and 0.2 gram portions used. Here no activity was shown unless manganous sulfate was added and air passed through for a considerable length of time.

In the experiments shown in Table II, the end point in titrating was taken to be the pink color which was permanent for at least 30 seconds. In some of the titrations the pink color faded in a few seconds and as there may have been a question as to the end points in these cases, a series of experiments was carried out in which the formol method of titrating was employed. The results are given in Table III. The treatment preliminary to the activity tests and until the titrations did not differ from the former experiments and the data concerning these, are shown in columns 1–5. The first part of the titrations was carried out like the titrations reported in Table II; alkali being added with phenolphthalein as indicator until a distinct pink was obtained; these results are given in columns 6–9 headed "Direct." Column 9 gives the amounts of action on direct titration. After the end point had been attained, 5–10 cc. of

TABLE III.—THE ACTION OF CASTOR BEAN LIPASE ON ETHYL BUTYRATE. FORMOL TITRATIONS.

	Expt. No.	Wt. of lipase. Gram.	Time of action of air. Hours.	Wt. of $MnSO_4.4H_2O$ added. Milligrams.	Time of action. Hours.	Activity tested. Cc. 0.1114 N NaOH used. Direct.				Formol total.		
						Ester water.	Lipase ester water.	Lipase water.	Action lipase ester.	Lipase ester water.	Lipase water.	Action lipase ester.
Not heated.....	32	0.2			43	0.08	2.67	0.75	1.84	2.99	1.14	1.77
Not heated.....	33	0.2	22		47	0.08	2.19	0.72	1.39	2.57	1.15	1.34
Not heated.....	34	0.2		20	43	0.10	2.87	0.87	1.90	3.26	1.17	1.99
Not heated.....	35	0.2	22	II 20	47	0.10	2.33	1.01	1.22	2.74	1.36	1.28
Heated.....	36	0.5			43	0.08	1.10	0.96	0.06	1.59	1.44	0.07
Heated.....	37	0.5	22		45	0.12	1.27	1.23	—0.08	1.86	1.80	—0.06
Heated.....	38	0.5		20	43	0.15	1.14	0.84	0.15	1.67	1.36	0.16
Heated.....	39	0.5	22	I 20	45	0.12	1.25	0.95	0.18	1.75	1.48	0.15

40% formaldehyde solution (neutralized toward phenolphthalein) was added and the titration continued until a distinct pink color was produced in the solution. In no case was any difficulty experienced in determining this end point. The total amounts of alkali required (*i. e.*, the amounts used in direct titration plus the amounts required after the addition of formaldehyde) are given in columns headed "Formol Total." In experiments 32–35, the lipase preparations were not heated with water preliminary to the treatments; in experiments 36–39, they were.

A comparison of experiments 32–35 with the results given in Table I shows a minor difference in the action of manganous sulfate in experiment 35, the action not being quite as great as would have been expected. The results given in Table I for this mixture are based upon a greater number of experiments than the result given in experiment 35, and this small difference need not be further considered. Experiments 36–39 show again a distinct increase in activity of the preparations in the presence of manganous sulfate after these had been inactivated by heat.

The important conclusion to be drawn from the results in Table III is that the same action is obtained by direct titration and by the total formol titration, as is shown by a comparison of the amounts of acid formed, indicated for each experiment in the last column. The difference between these two sets is less than 0.10 cc. in every case, a result within the experimental error of the titrations. This fact increases the probability that the results in Table II are correct, as the end points there and in the direct titrations of Table III were similar.

A number of 0.5 gram portions of lipase preparation were titrated to neutrality directly and then again after neutralized formaldehyde solution had been added. The mean values of the cc. 0.1114 *N* sodium hydroxide solution used were 0.45 cc. for the direct titration and 0.52 cc. additional after formaldehyde had been added. The same amount of lipase preparation heated to boiling with water for different lengths of time (1–4 hours) required slightly varying amounts of alkali in the direct titrations, but gave remarkably constant results for the additional amount of alkali required for neutralization after formaldehyde had been added, these results varying only between 0.52 and 0.55 cc. 0.1114 *N* sodium hydroxide solution. A similar result is shown in experiments 36–39. The amount of alkali required after addition of formaldehyde varied from 0.48 cc. to 0.57 cc. in the experiments in which no ester was present, and from 0.49 cc. to 0.59 cc. when ester was present, the presence or absence of manganous sulfate and the preliminary treatments exerting practically no effect. The experiments with 0.2 gram lipase preparation, not heated, showed a mean formol titration value of 0.23 cc. 0.1114 *N* sodium hydroxide solution. There is then no change in the number of amino and carboxyl groups neutralizing each other as shown by the formol titration results

when the lipase preparation was rendered inactive by heat or when it was activated again by the manganous sulfate.

In order to test the action of manganous sulfate and the lipase preparation in somewhat larger amounts, the experiments shown in Table IV were carried out. In experiment 40, a paper extraction thimble was placed in the mixture of 5 grams of lipase preparation, 250 cc. water and 5 grams of manganous sulfate. Activity tests on ethyl butyrate were made in the usual way with 10 cc. portions (slightly opalescent) taken from within the thimble, called "Solution" in the table, and with 10 cc. portions of the mixture outside the thimble, called "Mixture" in the table. After each successive removal of material for testing sufficient water was added to keep the total volume at 250 cc. and a current of air was passed through the increasingly dilute mixtures outside the thimble for the total lengths of time indicated. Columns 4–6 in the first part of the table show the treatment preliminary to testing the activities, and columns 2–9 under the heading "Activity Tested" give the results of the activity tests. The headings of the columns indicate, in sufficient detail, the significance of the results.

TABLE IV.—ACTION OF CASTOR BEAN LIPASE ON ETHYL BUTYRATE.

	Expt. No.	Wt. of lipase. Grams.	Water as solvent. Cc.	Time of action of air. (Total) hours.	Time of standing. (Total) hours.	Wt. of $MnSO_4.4H_2O$ present. Grams.
Not heated.....	40 *a*	5	250	4	..	5.0
	b			11	17	3.4
	c			17	34	2.4
Heated.....	41 *a*	5	250	..	..	...
	b			32	66	...
Heated.....	42 *a*	5	250	26	50	5.0
	b			32	66	3.4

ACTIVITY TESTED.

Expt. No. (*cont'd*).	Temperature of test.	Time of testing. Hours.	Part used for test.	Corresponding to wt. lipase preparation. Gram.	Cc. 0.1114 *N* NaOH used. Lipase ester water.	Ester water.	Lipase water.	Action lipase ester.
40 *a*.....	38°	19	Solution	0.2	0.40	0.04	0.14	0.22
			Mixture	0.2	1.02	0.04	0.47	0.51
b.....	38°	20	Solution	0.15	0.56	0.08	0.32	0.16
			Mixture	0.15	1.04	0.08	0.56	0.40
c.....	38°	22	Solution	0.12	0.38	0.06	0.16	0.16
			Mixture	0.12	0.75	0.06	0.41	0.28
41 *a*.....	38°	44	Solution	0.2	0.34	0.12	0.33	—0.11
b.....	38°	41	Solution	0.18	0.30	0.08	0.28	0
			Mixture	0.18	0.49	0.08	0.39	0.02
42 *a*.....	20°	21	Solution	0.2	0.80	0.14	0.51	0.15
	38°	21	Mixture	0.2	1.58	0.14	1.10	0.34
b.....	38°	41	Solution	0.15	0.55	0.16	0.37	0.02
			Mixture	0.15	1.57	0.16	0.69	0.72

Experiments 41 and 42 were carried out similarly, except that the activity of the lipase preparation was first destroyed by heating the mixtures for 2 hours at 100°. In experiment 41, no manganous sulfate was added; in experiment 42, 5 grams were added after heating and before the subsequent treatment.

Experiment 40 shows very little change in the activity of the lipase preparation in the presence of manganous sulfate, on passing air through the mixture and on standing, when the decreased amounts of lipase preparation in the later parts of the experiment are taken into account. Experiment 41 showed practically no activity after heating in the absence of manganous sulfate; while experiment 42 with similar treatment, but with manganous sulfate present, showed a marked activity, the first part approaching the value for the unheated lipase preparation. The second part showed an unaccountably high value for the activity of the mixture.

In discussing the results which have been given in the tables, the following points may be noted: In Tables I and II especially, the experiments given are in most cases, as was mentioned earlier in the article, the means of duplicate determinations; but besides these a large number of experiments were carried out, which are not given there, since essentially the same results were obtained. It may be remarked, however, that in some experiments, after the inactivated lipase preparation had been treated with manganous sulfate, much larger activities were shown than are recorded in any of the tables.

A comparative discussion of the reactivations and the original activity with regard to the magnitude of the effects would be of no value, since in neither case was any attempt made to obtain the conditions of maximum (or even comparable) activity by the addition of acid or other substance. Twenty milligrams of manganous sulfate ($MnSO_4.4H_2O$) added in experiments in Tables I–III were equivalent to 2.5% manganese of the lipase preparation with 0.2 gram of the latter, and 1.0% manganese with 0.5 gram. The molar concentrations of the solutions with regard to the manganese ranged from 0.0018 to 0.0036. Not enough experiments were carried out with varying amounts of manganese to show definit regularities.

Passing air through the solutions after manganous sulfate had been added appears to have no effect differing from that of allowing the solutions to stand in stoppered flasks. Probably enough air was dissolved in the solution and remained in contact with the mixtures to produce any oxidation if the latter was the cause of the observed effect. Carbon dioxide was not removed from the air before it was passed through the solutions; but since the blank experiments (without the addition of manganous sulfate) showed little or no action, it may be presumed that the carbon dioxide did not produce the observed effects.

The results in Table III indicate that there is no change in the number of amino and carboxyl groups neutralizing each other as shown by the formol titrations when the lipase preparation was inactivated by heat in aqueous solution or suspension, or when it was reactivated with the manganous sulfate.

The formation of acid in the treatments to which the preparations were subjected could not have been the cause of the observed activities, as the experiments where manganous sulfate was absent did not show the activities even with the increased acidities.

Attempts were made to use "oxygen carriers" other than manganous sulfate, but those tested, including ferrous sulfate, hydrogen peroxide, and potassium persulfate, showed themselves such marked hydrolytic action on the ester that the testing of the preparations after such treatment gave results of no value.

The main conclusion to be drawn from the experiments described is, that the castor bean lipase preparation after having been inactivated by heating with water was rendered active again to a small extent by manganous sulfate.

Theoretical.

Tanaka showed[1] that in the action of lipase from castor beans "acidity of the medium is non-essential to lipolytic hydrolysis." This agrees with the results of the first paper of this series[2] where a number of experiments were described in which different amounts of alkali were added to the castor bean preparation before the activity was tested, in order to make certain the absence of free acid in the medium initially.

In order to account for the accelerating action of manganous sulfate on castor bean lipase, as observed by Hoyer and by Tanaka and in the experiments described in the present paper, the following tentative explanation is offered: The inactive zymogen of lipase in castor beans is converted into the active enzyme by an oxidation reaction for which the presence of an "oxygen carrier" or catalytic agent is necessary. Simultaneous hydrolysis may or may not be involved in this reaction. The active enzyme is converted into inactive material by hydrolysis, slowly at low temperatures in aqueous solution or suspension, rapidly at higher temperatures. Presumably all of the substances involved in these changes, inactive zymogen, active enzyme, inactive product from enzyme, are protein in character.

The application of this explanation to the observed results is simple. Manganous sulfate, at any rate in the small amounts used in the experiments described in this paper, does not accelerate directly the action of the enzyme present, but by aiding the conversion of inactive zymogen into active enzyme increases the total amount of enzyme present, or makes

[1] *Loc. cit.*

[2] Falk and Nelson, THIS JOURNAL, 34, 735 (1912).

up for the enzyme which becomes inactive on account of hydrolysis, and therefore apparently accelerates the action. Heating the preparations with water hydrolyzes all of the active enzyme to inactive substance but evidently does not destroy all of the inactive zymogen present originally in the castor beans as the experiments showed a small activity of this heated material after treatment with manganous sulfate. The explanation of the results described here is, therefore, not that enzyme which had been inactivated was made active again, but that the preparation which had been inactivated still contained some zymogen from which active enzyme was again obtained.

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NOTE.

The Reaction between Calcium Permanganate and Ethyl Alcohol.—The following reaction, which was found accidentally, does not seem to be known and makes a good lecture experiment for demonstrating the oxidation of alcohol to aldehyde:

If several small fragments of calcium permanganate are dropped upon a porous plate moistened with a few cc. of ethyl alcohol, there will be a bright scintillation for an instant, and then the permanganate will be observed to glow quietly and steadily. This glowing may continue for upwards of five minutes and is accompanied by the evolution of fumes which are quite irritating to the eyes and suggestive of formaldehyde, acetaldehyde and acrolein. By drawing the fumes through warm ammoniacal solution of silver nitrate, a good reduction can be obtained, though without mirror formation.

This reaction together with that of Schwersenski and Caro[1] may be used as lecture experiments illustrating oxidation by permanganates. The specimens of methyl alcohol and acetone at hand do not react thus: isoamyl alcohol reacts somewhat less rapidly than ethyl.

F. ALEX. MCDERMOTT.

NEW BOOKS.

Essentials of Chemistry. By JOHN C. HESSLER AND ALBERT L. SMITH. Revised edition (1912) by John C. Hessler. New York: Benj. H. Sanborn & Co. Price, with manual $1.45, without manual, $1.25.

The 1912 revised Hessler and Smith is an up-to-date, accurate textbook of chemistry, of convenient size, and excellent typography. The book presents a very large assemblage of facts whose relative importance is set forth by a liberal use of italics and several kinds of type. Numerous cross references inter-connect all parts of the text. Chapter XV on

[1] *Chem. Ztg.*, **22**, 58 (1898); *Scientific American*, **1912**, 225.