tion of the alkaloid and after filtration the colorless filtrate was titrated with standard acid.

Calculated: Ti, 6.24; F, 14.80; H_2O, 9.30.
Found: Ti, 6.56; F, 15.24; H_2O, 9.54.

Aniline Titanium Fluoride, $(C_6H_5NH_2)_2.H_2TiF_6.H_2O$.—Pink colored needles, readily soluble in water and in alcohol. The salt became perfectly anhydrous after standing for a period of three months, exposed to the air.

Calculated: Ti, 13.05; F, 30.96.
Found: Ti, 12.99; F, 30.88.

Piperine and santonine apparently do not form double fluorides with titanium.

Numerous attempts were made, both by the boiling point and freezing point method, to arrive at the molecular magnitudes of these several double salts but the results were quite discordant.

In conclusion, it may be mentioned that the titanic acid used in this study was derived from rutile from Magnet Cove, Arkansas, and that this particular sample of mineral contained quite a considerable quantity of vanadium.[1]

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE USE OF THE ROTATING ANODE IN ELECTROLYTIC SEPARATIONS.[2]

BY MARY E. HOLMES.

Received September 3, 1908.

This investigation was undertaken with the view of learning what advantages could be had with the rotating anode, when using low currents. Heretofore, currents of from three to five amperes have been employed when using the rotating anode. The most exhaustive contribution to the subject of metal separations, employing the rotating anode, was made by Ashbrook in 1904.[3] All his work was done with high currents, five amperes being generally used. Other separations were later recorded by Miss Langness (Thesis, 1906), in which low currents and rotation were successful. The results would seem to indicate the possibility of obtaining other separations with low currents in comparatively short periods of time.

Criticism of the rapid methods of electrolytic work has often been made to the effect that while the methods employed may be adequate for the determination of single metals, the introduction of more than one metal

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[1] *Compt. rend.*, **53**, 161 (1861); *Astrophysical Jour.*, **6**, 22 (1897).

[2] From the author's thesis for the Ph.D. degree.

[3] THIS JOURNAL, **26**, 1285.

into the solution causes such a variation in conditions that separations are not practicable. The only answer to such doubts is a systematic study of the whole subject of separations, varying condition of current, rotation, time and electrolyte used, so that for each metal all possibilities may be determined. This communication represents a beginning of such study made with the element cadmium. The possibilities of its separation with low currents from the metals of Groups III and IV, and from magnesium have been ascertained, and a comparison made of these results with those previously obtained with high currents.

The conditions of work were as follows: The current was kept in almost all cases below one ampere. Currents below 0.3 or 0.4 ampere were not found useful. The rotating dish anode used first by Miss Langness (Thesis, 1906) was employed. The cathode was a platinum dish of 200 cc. capacity, the usual form of dish employed in electro-analysis. The time required for a determination was from forty-five minutes to one hour, and the electrolytes used were (1) sulphuric acid, and (2) ammonium acetate and acetic acid.

Experimental Part.

A. Sulphuric Acid Electrolyte.

1. *Precipitation of Cadmium Alone.*—A solution of cadmium sulphate was used, containing about 0.2 gram of cadmium in 10 cc. The first problem was the determination of the lowest possible current at which the cadmium could be completely precipitated. Varying quantities of sulphuric acid were tried, the best results being obtained with 0.5 to 1 cc. of acid, specific gravity 1.09. The solution was not heated before electrolysis. Ten cc. of the solution were placed in the platinum dish, the desired amount of sulphuric acid added, the solution diluted to 60 cc., and then electrolyzed at room temperature. The volume of solution should not exceed 60-65 cc. when the dish anode is used, in order that splashing may be avoided. A speed of 300-400 revolutions a minute gave the best results. The deposits were smooth and adherent.

RESULTS.

	$CdSO_4$ Cd in grams.	H_2SO_4, sp. gr. 1.09. cc.	$N.D._{100}$ amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.2070	1	0.1	2.5	4 hr. 10 m.	0.1959	—0.0111
2.	0.2070	1	0.2	2.75	45 m.	0.1625	—0.0445
3.	0.2070	1	0.3	2.75	1 hr. 20 m.	0.2068	—0.0002
4.	0.2070	1	0.3	2.75	1 hr. 15 m.	0.2067	—0.0003
5.	0.2070	1	0.3	2.75	45 m.	0.2063	—0.0007
6.	0.2070	1	0.3	2.75	45 m.	0.2069	—0.0001
7.	0.2070	1	0.3–0.4	3	45 m.	0.2074	+0.0004

It was, therefore, concluded that with a current of 0.3 ampere, complete precipitation of the cadmium could be obtained in forty-five minutes.

2. *Separation of Cadmium from Metals of Group III.* (*a*) *From Aluminium.*—Ten cc. of cadmium sulphate solution and 25 cc. of aluminium sulphate solution (0.1811 gram aluminium in 25 cc.) were placed in the platinum dish, 1 cc. sulphuric acid (sp. gr. 1.09) added, and the electrolysis conducted at room temperature.

	$CdSO_4$ Cd in grams.	$Al_2(SO_4)_3$ Al in grams.	H_2SO_4, sp. gr. 1.09. cc.	N.D.$_{100}$, amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.2051	0.1811	1	0.4	3	45 m.	0.2052	+0.0001
2.	0.2051	0.1811	1	0.4	2.75	45 m.	0.2051	+0.0000
3.	0.2051	0.1811	1	0.4	2.75	45 m.	0.2054	+0.0003
4.	0.2051	0.1811	1	0.4–0.5	2.75	45 m.	0.2047	—0.0004
5.	0.2051	0.1811	1	0.4–0.5	2.75	45 m.	0.2047	—0.0004
6.	0.2051	0.1811	1	0.4–0.5	2.75	45 m.	0.2051	0.0000

Similar results were obtained by Ashbrook, using high currents.

(*b*) *From Chromium.*—The experiments with chromium were not as conclusive. The amount of cadmium deposited at 0.4 ampere was uncertain. With a current of 0.7 ampere, the deposits were too high in weight, but after treating them with hot water, the weight became less, in some cases reaching the theoretical amount. The deposits were somewhat dark and irregular in appearance. They evidently occluded mother liquor, for on treating one deposit with nitric acid, and evaporating the solution to dryness, a greenish residue was obtained. No decisive test for cadmium was obtained from the filtrates of Experiments 4 and 5.

	$CdSO_4$ Cd in grams.	$Cr_2(SO_4)_3$ Cr in grams.	H_2SO_4, sp. gr. 1.09. cc.	N.D.$_{100}$, amperes.	Volts.	Time.	Cd found	Error in grams.
1.	0.2051	0.2635	0.5	0.4	2.8	1 hr.	0.2052	+0.0001
2.	0.2051	0.2635	0.5	0.4	2.5	45 m.	0.1081	—0.0970
3.	0.2051	0.2635	0.5	0.4–0.5	2.5–3	1 hr.	0.1696	—0.0355
4.	0.2051	0.2635	0.5	0.4–0.75	3—4	1 hr.	0.2065	
				after washing with hot water			0.2053	+0.0002
5.	0.2051	0.2635	0.5	0.4–0.55	2.75–3	1 hr.	0.2065	
				after washing with hot water			0.2057	+0.0006
6.	0.1936	0.2763	0.5	0.7	3	1 hr.	0.1955	
				after washing with hot water			0.1952	+0.0016

Ashbrook attempted to separate cadmium from chromium, using high currents, but states that in sulphuric acid solution, the deposit always weighed low. With phosphoric acid, however, he did get a successful separation.

(*c*) *From Iron.* 1. *Ferric Iron.*—No satisfactory separation of cadmium from ferric iron was obtained with the conditions used with chromium. The iron tends both to hold back the cadmium, and to be partially precipitated by that metal.

2. *Ferrous Iron.*—It is evident from a series of results, that with low currents, the separation of cadmium from iron in a sulphuric acid electrolyte is not a success. An entirely successful separation of these two

metals was obtained by Miss Davison (Thesis, 1905) in twenty or twenty-five minutes, using a potassium cyanide electrolyte and a current of five amperes. With the same current, Ashbrook found the separation possible in ten minutes, both in sulphuric acid and phosphoric acid solution.

3. *Separation of Cadmium from Metals of Group IV.* (*a*) *From Cobalt.*—No deposit of cobalt was obtained by electrolyzing a solution containing 0.1808 gram of cobalt at 0.4 ampere and 2.5 volts for one hour and twenty-five minutes. Satisfactory separations of cadmium from cobalt were then made, as shown by the following data:

	$CdSO_4$ Cd in grams.	$CoSO_4$ Co in grams.	H_2SO, sp. gr. 1.09. cc.	$N.D._{100}$, amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.2051	0.1808	1	0.4	2.5	45 m.	0.2048	—0.0003
2.	0.2051	0.1808	1	0.4–0.5	2.5–2.75	45 m.	0.2051	0.0000
3.	0.2051	0.1808	1	0.4–0.5	2.5–3	45 m.	0.2055	+0.0004
4.	0.2051	0.1808	1	0.4–0.5	2.5–2.9	45 m.	0.2045	—0.0006

In contrast to the results under iron, the use of a low current makes possible a separation of cadmium from cobalt which is not obtained with high currents. Ashbrook tried this separation, but found that in both sulphuric and phosphoric acid solution, cobalt was partially precipitated. Miss Davison tried the separation of cadmium from cobalt in cyanide solution, but found that the separation was not complete, even after thirty-five minutes. Here, even with the low current of 0.4 ampere, the precipitation is complete in forty-five minutes. With stationary electrodes, the separation of cadmium takes place using a still lower current, 0.078 ampere, but four to four and a half hours are required.

(*b*) *From Nickel.*—The most favorable conditions and results follow:

	$CdSO_4$ Cd in grams.	$NiSO_4$ Ni in grams.	H_2SO_4, sp. gr. 1.09. cc.	$N.D._{100}$, amperes.	Volts.	Time.	Cd found.	Error in grams
1.	0.2070	0.1630	1	0.3	2.5+	45 m.	0.2067	—0.0003
2.	0.2070	0.1630	1	0.3	3.25	45 m.	0.2073	+0.0003
3.	0.2070	0.1630	1	0.3	2.75	45 m.	0.2074	+0.0004

Miss Davison, working with the cyanide electrolyte, always found some nickel in the cadmium deposit. Ashbrook had the same experience when using phosphoric acid solution, but obtained a satisfactory separation with sulphuric acid as electrolyte, using a current of 5 amperes.

(*c*) *From Manganese.*—The results indicate that high currents are best for this separation, since Ashbrook separated cadmium completely from manganese, both in phosphoric and sulphuric acid solution, using a current of five amperes.

The possibility of formic acid as an electrolyte for this separation was then considered, as formic acid is one of the best electrolytes for cadmium and for manganese when determined singly. It proved to be successful. The deposits of cadmium obtained were especially beautiful, soft and velvety in appearance, and of changing shades of silver gray.

	$CdSO_4$ Cd in grams.	$MnSO_4$ Mn in grams.	Formic acid. cc.	$N.D._{100}$, amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.2051	0.2421	5	0.4–0.5	2.5–3	1 hr.	0.2053	+0.0003
2.	0.2051	0.2421	5	0.4	2.5	1 hr.	0.2058	+0.0007
3.	0.2051	0.2421	5	0.4	2.5	1 hr. 25 m.	0.2051	0.0000
4.	0.2051	0.2421	5	0.4	2.75	45 m.	0.2045	—0.0006

(*d*) *From Zinc.*—A satisfactory separation of cadmium from zinc was obtained. No deposit of zinc appeared in the electrolysis of 10 cc. of zinc sulphate solution containing 0.2094 gram of zinc, using a current of 0.4 ampere for forty-five minutes. Separations of cadmium from zinc were then tried under the same conditions. The deposits were dissolved in nitric acid and tested for zinc on charcoal with the blowpipe, fusing with sodium carbonate and moistening with cobalt nitrate. Zinc was not found and the filtrates were free from cadmium.

	$CdSO_4$ Cd in grams.	$ZnSO_4$ Zn in grams.	H_2SO_4, sp. gr. 1.09. cc.	$N.D._{100}$, amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.2050	0.2094	1	0.4	2.75–2.9	45 m.	0.2053	+0.0003
2.	0.2050	0.2094	1	0.4	3	45 m.	0.2057	+0.0007
3.	0.2050	0.2094	1	0.4	2.75	45 m.	0.2057	+0.0007
4.	0.2050	0.2094	1	0.4	2.75	45 m.	0.2050	0.0000
5.	0.2050	0.2094	1	0.4	3	45 m.	0.2048	—0.0002

Ashbrook observed that "zinc always came down with the cadmium in sulphuric acid solution, and also in phosphoric acid solution." This is another case like the cadmium-cobalt separation, in which a low current is successful where a high current has failed. Here, again, the separation may be obtained with stationary electrodes, and has been worked out with various electrolytes, but the time required is from three to ten hours.

(*e*) *From Magnesium.*—The experiments on these two metals also resulted in a satisfactory separation.

	$CdSO_4$ Cd in grams.	$MgSO_4$ Mg in grams.	H_2SO_4, sp. gr. 1.09. cc.	$N.D._{100}$, amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.2051	0.1785	0.5	0.4–0.5	3	45 m.	0.2055	+0.0004
2.	0.2051	0.1785	0.5	0.4–0.5–0.6	3	50 m.	0.2053	+0.0002
3.	0.2051	0.1785	0.5	0.4	2.7	1 hr. 5 m.	0.2051	0.0000

Similar results were obtained by Ashbrook with magnesium, using high currents.

B. *Acetate Electrolyte.*

The electrolyte used in these determinations was 1 gram of ammonium acetate together with 0.5 cc., or more often 1 cc., of acetic acid, 1 : 3 by volume (1 volume glacial acetic acid to 3 of water). The solutions were heated to just below boiling before electrolyzing. This preliminary heating was found to be quite necessary, influencing the character of the deposit to a considerable extent. The deposits of cadmium from the acetate electrolyte are more coarsely crystalline than from the sulphuric acid electrolyte, and hence sometimes not adherent. If proper care is exercised, however, there need be no loss of metal. Cold water was used in washing the deposits, as in the other set of determinations.

I. Precipitation of Cadmium Alone.

	$CdSO_4$ Cd in grams.	1 g. $NH_4C_2H_3O_2$ $C_2H_4O_2$(1:3). cc.	$N.D._{100}$ amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.2051	0.5	0.05	2.25	20 m.	No deposit	
2.	0.2051	0.5	0.1	2.5	25 m.	Trace of deposit	
3.	0.2051	0.5	0.15	2.7	1 hr.	0.2040	—0.0011
4.	0.2051	1	0.2	2.5	2 hrs. 30 m.	0.2054	+0.0003
5.	0.2051	1	0.2	2.5	1 hr. 5 m.	0.2041	—0.0010
6.	0.2051	1	0.05–0.3	2.3–3	1 hr.	0.2051	0.0000
7.	0.2051	1	0.3	3	1 hr.	0.2048	—0.0003
8.	0.2051	1	0.3	2.75	1 hr.	0.2052	+0.0001

0.3 ampere was, therefore, taken as the current to be used for further work. The time can be reduced to forty-five minutes.

II. Separation of Cadmium from Metals of Group III.

(*a*) *From Aluminium.*—It was in the course of the work on these separations that the necessity of heating the solutions before electrolysis was made evident. Several separations of cadmium from aluminium, and several determinations of cadmium alone, were tried at ordinary temperature. The weight of metal was invariably high, the deposit containing coarse crystals, and having a tendency to sponginess, and hence occluding mother liquor. On heating the solutions, however, the deposits were adherent, and not spongy, and the results were satisfactory. The difference in deposits from cold and hot solutions is shown as follows:

COLD.

	$CdSO_4$ Cd in grams.	1g. $NH_4C_2H_3O_2$ $C_2H_4O_2$(1:3). cc.	$N.D._{100}$ amperes.	Volts.	Time.	Cd found.	Error in grams.
1.	0.1936	1	0.3	2.8	1 hr.	0.2000	+0.0064
2.	0.1936	1	0.3	3.	50 m.	0.1940	+0.0004
3.	0.1936	1	0.3	2.9	45 m.	0.1936	0.0000
4.	0.1936	1	0.3	2.8	45 m.	0.1951	+0.0015
5.	0.1936	1	0.3	3.	45 m.	0.1941	+0.0005

In experiment 3, the deposit was washed with hot water before weighing.

HOT.

6.	0.1936	1	0.3	3.	45 m.	0.1938	+0.0002
7.	0.1936	1	0.3	2.5	45 m.	0.1936	0.0000

$CdSO_4$ $Al_2(SO_4)_3$ 1g. $NH_4C_2H_3O_2$

	Cd in grams.	Al in grams.	$C_2H_4O_2(1:3)$. cc.	$N.D._{100}$. amperes.	Volts.	Time.	Cd found.	Error in grams.
				Cold.				
1.	0.1936	0.1811	1	0.3	2.7–3.2	45 m.	0.1964	+0.0028
2.	0.1936	0.2200	1	0.3	2.7	45 m.	0.1958	+0.0022
				Hot.				
3.	0.1936	0.2200	1	0.3	2.75	45 m.	0.1934	—0.0002
4.	0.1936	0.2200	1	0.3	3.	45 m.	0.1941	+0.0005
5.	0.1936	0.2200	1	0.3	2.5	45 m.	0.1946	+0.0011
6.	0.1936	0.2200	1	0.3	2.75	45 m.	0.1932	—0.0004

Experiment 5 shows that high results may be obtained even when the solution is heated before electrolysis.

(*b*) *From Chromium.*—No satisfactory separation of cadmium from chromium was obtained in this electrolyte.

(*c*) *From Iron.* 1. *Ferric Iron.*—As in the case of chromium, no satisfactory results were obtained. The same variation in the electrolyte was employed as under chromium, ammonium acetate alone, acetic acid alone, and the combination of the two. The current was varied from 0.3 to 0.9 ampere. The deposits were spongy and dark, with traces of basic salt. They had the appearance of containing iron, and always gave evidence of that metal by the sulphocyanate test.

2. *Ferrous Iron.*—One gram of ferrous sulphate was used, and the customary amount of ammonium acetate and acetic acid. In two experiments, using 0.3 ampere for forty-five minutes, the following results were obtained:

Cd present.	Cd found.	Error in grams.
0.1936	0.1930	+0.0044
0.1936	0.1819	—0.0117

One deposit was high, the other low in weight, but both had the appearance of containing iron, and both gave tests for that metal.

III. Separation of Cadmium from Metals of Group IV.

(*a*) *From Cobalt.*— When a solution of cobalt sulphate (0.1808 g. cobalt) was subjected to electrolysis with 0.3 ampere in the acetate electrolyte (1 g. ammonium acetate and 1 cc. acetic acid 1 : 3), the solution turned brown, indicating oxidation, and there was a slight metallic deposit on the cathode and also on the anode. These deposits dissolved in nitric acid, the heavier cathode deposit giving a pink solution, the anode deposit a colorless solution. Sodium hydroxide, however, gave a dark precipitate with this colorless solution, and on testing this precipitate with a borax bead, a blue color was obtained. Hence both deposits were evidently cobalt.

	$CoSO_4$ Co in grams.	1g. $NH_4C_2H_3O_2$ $C_2H_4O_2(1:3)$. cc.	$N.D._{100}$, amperes.	Volts.	Time.	Co found.
1.	0.1808	1	0.3	2.0–2.25	1 hr.	0.0176
2.	0.1808	1	0.3	2.5–3	1 hr.	0.0339

Therefore, no separation of cadmium from cobalt could be expected under these conditions.

(*b*) *From Nickel.*—Similar results were obtained with nickel.

(*c*) *From Manganese.*—The rotating dish cathode was again employed, but the weight of the metal was always low. The deposits were adherent and finely crystallized, but had none of the velvet-like appearance given by the formic acid electrolyte.

	$CdSO_4$ Cd in grams.	$MnSO_4$ Mn in grams.	1g. $NH_4C_2H_3O_2$ $C_2H_4O_2$(1:3). cc.	$N.D._{100}$ amperes.	Volts.	Time.	Cd found.	Error. in grams.
1.	0.1936	0.2421	1	0.3	1.5–2.5	45 m.	0.1907	—0.0029
2.	0.1936	0.2421	1	0.3	1.5–2.5–3.2	45 m.	0.1893	—0.0043
3.	0.1936	0.2421	1	0.3	1.5–3	1 hr.	0.1869	—0.0067

(*d*) *From Zinc.*—As in the case of cobalt and nickel, zinc begins to be deposited with such low currents in an acetate electrolyte that no separation of cadmium from zinc is possible with 0.3 ampere.

(*e*) *From Magnesium.*—This separation was successful.

The question arose as to how much the particular form of anode used in this work influenced the time necessary for a determination. The dish anode should reduce the time factor greatly, judging from its action in previous work. To answer this question more definitely, the spiral anode was substituted in a determination of cadmium from 10 cc. of cadmium sulphate solution, containing 0.1936 g. cadmium. One cc. sulphuric acid (1.09) was used as the electrolyte, and 0.4 ampere as the current. After forty-five minutes, the current was interrupted. The deposit of cadmium obtained weighed only 0.1742 g., proving the complete precipitation of the metal by use of the spiral anode would require more time than by use of the dish anode.

The object of this investigation, as previously stated, was *first*, to prove whether satisfactory separations of metals could be made with the rotating anode using low currents, and *second*, to throw some light on the question whether the rapid methods of electrolysis are of practical value in conducting separations.

The first question is certainly answered in the affirmative. Separations of cadmium were made from aluminium, chromium, cobalt, nickel, zinc, and magnesium, with the sulphuric acid electrolyte, from manganese with formic acid as electrolyte, and from aluminium and magnesium with the acetate electrolyte.

As to the practical value of the work, a comparison should be made of these results with the results obtained with stationary electrodes, and with the rotating anode, using high currents. This is best made in tabular form

TABLE I.

Sulphuric acid electrolyte separations of Cd from

	Stationary electrodes.		Rotating anode			
			Low currents.		High currents.	
	Ampere.	Time.	Ampere.	Time.	Ampere.	Time.
Al	0.078	4–4½ hrs.	0.4	45 min.	5	10 min.
Cr	0.078	4–4½ hrs.	0.4	1 hr.	Not successful	
Fe	0.078	4–4½ hrs.	Not successful		5	10 min.
Co	0.078	4–4½ hrs.	0.4	45 min.	Not successful	
Ni	0.078	4–4½ hrs.	0.3	45 min.	5	10 min.
Mn	0.078	4–4½ hrs.	Not successful		5	10 min.
Zn	Not recorded		0.4	45 min.	Not successful	
Mg	Not recorded		0.4	45 min.	5	10 min.

TABLE II.

Separations of Cd from

	Phosphoric acid electrolyte. High currents.		Acetate electrolyte. Low currents.	
	Amperes.	Time.	Ampere.	Time.
Al	5	10 min.	0.3	45 min.
Cr	5	10 min.	Not successful	
Fe	5	10 min.	Not successful	
Co	Not successful		Not successful	
Ni	Not successful		Not successful	
Mn	5	10 min.	Not successful	
Zn	Not successful		Not successful	
Mg	5	10 min.	0.3	45 min.

	Formic acid electrolyte. Low currents.	
	Ampere.	Time.
Mn	0.4	1 hr.

Table I shows, at once, the advantage of rotation, even with low currents, over stationary electrodes. A comparison of Tables I and II brings out the following points in regard to rotation with high and with low currents.

1. Separations of cadmium from aluminium and magnesium are possible in all cases studied.

2. The best conditions for the separation of cadmium from chromium were with a high current and phosphoric acid as electrolyte, although the separation is possible with a low current in sulphuric acid solution.

3. The separation of cadmium from iron is possible with a high current, but not with a low current.

4. Separations of cadmium from cobalt and zinc are possible with a low current, but not with a high current.

5. The separation of cadmium from nickel is possible with both a high and a low current, but the first is to be preferred.

6. The separation of cadmium from manganese is best made with a

high current, but may be made with a low current, if formic acid is the electrolyte.

This study is, of course, only a fragment of what remains to be done.

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INVESTIGATION OF THE CLAISEN CONDENSATION. III. FURTHER CONTRIBUTIONS TOWARDS THE ELUCIDATION OF THE MECHANISM OF THE REACTION.[1]

BY J. BISHOP TINGLE AND ERNEST E. GORSLINE.

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The various current theories regarding the mechanism of the ethyl acetoacetate condensation were discussed in our second paper. It is, therefore, only necessary in the present communication to state that, broadly, the question is whether the sodium, or other condensing agent, acts directly on the ethyl acetate, or whether it reacts first with a trace of alcohol, the actual condensation being brought about by the sodium ethylate so produced. It is evident that valuable evidence on the question at issue might be obtained by an examination of the behavior of ethyl acetate free from alcohol. Accordingly, our early efforts were directed towards the purification of this ester. The product which we eventually obtained was probably the purest specimen of this compound hitherto prepared. It reacted with sodium, to form ethyl acetoacetate, as readily as the ordinary "pure" material.

We think that this effectively disposes of the idea that the action is caused by the presence of a trace of alcohol in the ester, unless, of course, the statement be made that ethyl acetate is *always* dissociated to some infinitesimal extent into alcohol, or into some hypothetical "ethylidene," or "active variety of ethylene," whatever these may be. Statements of this nature, though they are made not infrequently, are outside discussion, because they assume the very point at issue.

Much work has been done by A. Michael, Nef and others on the purification of ethyl acetate and also on the quantity of hydrogen evolved from sodium and ethyl acetate. This quantity is not equivalent to that of the reacting sodium. A portion of the gas always attacks certain of the other substances which are present.

We have carried out a very large number of experiments with the object of eliminating as far as possible the effect of this absorbed gas. We added to the reacting materials a number of easily reducible substances in the hope that the hydrogen would attack them in preference to reacting with the ethyl acetate derivatives. Our results were not very encouraging.

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[1] Our previous papers of this series appeared in the *Am. Chem. J.*, **37,** 483 (1907); **40,** 46 (1908).