ON THE RELATION OF CHEMICAL ACTIVITY TO ELECTROLYTIC CONDUCTIVITY.

BY JOHN LANGLEY SAMMIS

Introduction

The recognition of the fact that electrical and chemical phenomena may accompany each other under certain conditions, dates back to the time of Volta. Faraday demonstrated that the amount of chemical change effected and the amount of electric current which simultaneously passes through an electrolyte, bear a constant ratio to each other. From the vast majority of chemical changes known, we are at present unable to produce electricity directly; and it is equally true, that only in a very limited number of cases is it possible to effect chemical decomposition by direct application of the electric current. Nevertheless, since the time of Sir Humphry Davy, who originated the first electrochemical theory, there has been a lingering notion among chemists and physicists that all chemical action is essentially electrical in character. This idea has been rather vague and ill-defined; and it must be confessed that while it dominated in the dualistic system of Berzelius, it was forced into the background with that system by the development of organic chemistry. Of recent years through the rise of physical chemistry, the same notion has again come forward in somewhat modified form. The intensive study of the conductivity of electrolytes and of the rates with which chemical reactions proceed in homogeneous liquids that are capable of being decomposed by the direct agency of the electric current has led to the idea that chemical activity and electrolytic conductivity go hand in hand and are proportional to each other. In the language of the theory of electrolytic dissociation of Arrhenius, chemical action is supposed to take place between charged particles, or ions, which are considered as existing in the reacting bodies; and thus, since in a given case electrical conduction is supposed to be proportional to the number of ions present, and the rate of chemical action would also be determined by the number of ions per unit of volume, the relation between electrical conductivity and chemical activity would be explained. It is unnecessary to dwell on this matter further, here, since it is fully set forth in the various books on the electrolytic dissociation theory and on physical chemistry which have appeared in recent years.

The question that naturally arises in considering whether there is an interdependence between chemical activity and electrolytic conductivity is twofold in nature. (1) In the case of a reaction which proceeds in a conducting liquid, is it possible to vary independently of each other within considerable limits the conductivity of the liquid and the rate of the chemical change? (2) Is it possible to produce all types of chemical reactions in liquids that are insulators as well as in liquids that are electrolytes? It is the purpose of this paper to take up the consideration of these questions from the experimental standpoint. While the first question raised has not hitherto been subjected to rigid direct test, a considerable amount of conclusive work has already been done on the second by Kahlenberg,[1] who showed that instantaneous chemical reactions, exactly like those that take place in solutions which are excellent electrolytes, may also go on in solutions that are the very best of insulators. So far as the second question is concerned, then, the work consisted of gathering experimental data in addition to those already collected by Kahlenberg; and in the course of this line of investigation it was found for the first time that it is indeed possible to replace one metal with another by direct action in insulating liquids, exactly as it is possible to accomplish this in conducting liquids. This discovery enables us to state that all reactions which take place in liquids that conduct the current may be reproduced as to type in liquids that are the best of insulators. In the study of the first

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[1] "Instantaneous Chemical Reactions and the Theory of Electrolytic Dissociation," Jour. Phys. Chem., 6, 1 (1902).

question raised, the reactions whose rates were measured were the inversion of sugar, the catalysis of methyl acetate, and the solution of metallic magnesium in dilute acids. The acids used were nitric, hydrochloric and acetic. In order to reduce the conductivity after the first measurements had been made, similar solutions were prepared, in which an equal volume of benzol was substituted for part of the water present before, maintaining the percentages of acid and sugar or ester unchanged. While benzol is practically insoluble in aqueous sugar solutions, yet in the presence of sufficient acetic acid to invert the sugar at a rate convenient for measurement, a considerable proportion of the water can be replaced by benzol without causing two layers to form. The same end was reached in the other solutions, where nitric or hydrochloric acid was present instead of acetic, by using a mixture of water and acetone as a solvent. It was found in every case studied, that the substitution of benzol for part of the water, produced changes in the rate of chemical action and in conductivity which were entirely out of proportion to each other and not even always in the same direction.

Relation between Rate of Reaction and Electrolytic Conduction

(1) A solution (B) containing 29.4 grams of cane sugar in 57 cc of water at 25° C was mixed with 113.6 grams of glacial acetic acid, and the time of mixing was recorded. This solution was kept in a large Ostwald thermostat, containing a thermometer graduated to tenths of a degree, a thermoregulator and a stirrer. From time to time, the solution was examined in the polariscope, using an observation tube two decimeters long, surrounded by a water-jacket through which ran water at 25° C, during the observations. The instrument employed was of the Landolt-Lippich type made by Schmidt and Haensch and could be read by the vernier to 0.01 circular degree. The polariscope readings given below are each the average of six or more settings, and the time recorded is the number of minutes which had elapsed

from the time of mixing to the middle of the short period, during which the six successive settings were made. Shortly after the first polariscope observation was made, a portion of the solution was placed in a conductivity cell having circular platinized platinum electrodes about one centimeter apart and 2.5 centimeters in diameter and the conductivity was determined at 25° C. At the same time as the first, a second solution (A) was prepared, containing the same amount of sugar and glacial acetic acid as in (B), together with 36.2 cc water and 20 cc of benzol. The proportions in which these liquids are consolute have been determined by A. T. Lincoln.[1] The two solutions (A) and (B) were kept together in the thermostat, and examined alternately in the same polariscope tube, which was carefully washed and dried each time before use.

TABLE I

Solution (A)	Solution (B)
29.4 grams cane-sugar	29.4 grams cane-sugar
113.6 grams acetic acid	113.6 grams acetic acid
36.2 cc water	57.0 cc. water
20.0 cc benzol	—
Conductivity at 25° C	—
45.0×10^{-6}	218.0×10^{-6}

POLARISCOPE READINGS.

Time	Rotation	Time	Rotation
7 min.	19°.31	4 min.	18°.74
65 "	18.56	52 "	18.45
125 "	18.29	128 "	18.07
185 "	18.24	162 "	17.77
245 "	17.52	225 "	17.15
308 "	17.00	282 "	16.82
395 "	16.87	356 "	16.58
510 "	16.36	492 "	15.85
3510 "	12.04	3552 "	11.45
9600 "	3.66	9642 "	2.10

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[1] Jour. Phys. Chem., 8, 248 (1904).

During the last two periods of time, the temperature of the thermostat varied somewhat, and the solutions, of course, underwent equal variations.

Change of rotation in		Change of rotation in	
510 min.	2°.95	492 min.	2°.89
3510 "	7°.27	3552 "	7°.29
9600 "	15°.65	9640 "	16°.64

The viscosity of these solutions at 25° C, was compared with that of water in a viscosimeter of the form described by Ostwald.[1] The specific gravity of solution (A) was 1.102, and

Time for water to flow out.........	2 min.,	13.7 sec.
Time for solution (A)..............	10 "	47.2 "
Time for solution (B)..............	10 "	2.2 "

that of solution (B) was 1.121 at 25° C. The small difference of viscosity in the solutions shows that this property is not to be held to account for the wide difference of electrical conductivity manifested by the solutions.

Ratio of the conductivities................	4.8 to 1
Ratio of the rates of inversion............	1 to 1

The use of benzol in solution (A) has reduced the conductivity in the ratio of 4.8 to 1, but did not materially affect the rate at which the inversion proceeded.

(2) In preliminary experiments with magnesium ribbon, it was found that several pieces cut from the same part of a strip, do not evolve hydrogen at a uniform rate when immersed in the same solution. In all the experiments with magnesium described below a cast bar of the metal was employed, which was found to act quite uniformly. This bar was 4.1 cm long and had a cross section of about 0.3 sq. cm. After cleaning the piece, it was dropped into an acid solution for ten minutes or so, while the hydrogen was being evolved and collected, then it was quickly removed, washed, and dried with filter paper, using care not to abrade the surface, and was ready for use in another solution. The effect of small changes of

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[1] Hand- und Hülfsbuch, 1902, page 260, Fig. 168.

temperature upon the rate of such actions is marked.[1] The acids used were placed in bottles carrying thermometers graduated to tenths of a degree, and kept in a large thermostat also containing a thermometer, and cooled to 7° C. The magnesium was then dropped into the acid, a stop-watch was started, and the bottle was shaken steadily in the thermostat, as the action proceeded. The hydrogen evolved each minute was collected separately, so that any irregularities could be detected. Three acid solutions were prepared and the same bar of magnesium was dropped alternately into each. The experiments are numbered in the order in which they were performed.

Solution (A) was made of 68 cc glacial acetic acid and 32 cc of water. Its specific conductivity was 61×10^{-4}.

Solution (B) consisted of 68 cc of glacial acetic acid, 10.5 cc benzol and 20.5 cc of water. Its conductivity was 30×10^{-4}.

Solution (C) was composed of 34 cc of glacial acetic acid and 66 cc of water. Its specific conductivity was 76×10^{-4}.

During five minutes, the rise of temperature caused by the chemical action in the acid bottle was 1.5° to 2.0° in solutions (A) and (B), and about 5.0° in solution (C).

The use of benzol in solution (B) has decreased its conductivity to less than one-half that of (A), yet its action upon the metal has been diminished by only about 20 percent.

Comparing solutions (A) and (C), it is apparent that the use of more water in (C) has increased the chemical activity of that liquid toward magnesium to about 625 percent of that of (A), while at the same time the specific conductivity has been increased by only 25 percent. If the same solutions had not been used, but fresh ones prepared, the differences between 6, 7 and 9 would disappear, and further emphasize the conclusions drawn.

(3) Another experiment, similar to the last, was performed, using different acid solutions. Solution (A) consisted

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[1] Cf. Spring: Bull. Soc. Chim., Paris (3), 3, 181 (1890).

of 50 cc of glacial acetic acid and 50 cc of water. Solution (B) was composed of 50 cc glacial acetic acid, 25 cc acetone, and 25 cc of water. The same bar of magnesium was used as before.

TABLE II

VOLUME OF HYDROGEN EVOLVED BY ONE AND THE SAME BAR OF MAGNESIUM FROM

Time	Solution (A) Experiment No.			Solution (B) Experiment No.			Solution (C) Experiment No.		
	2 cc	4 cc	8 cc	1 cc	3 cc	5 cc	6 cc	7 cc	9 cc
0.5 min.	—	—	—	—	—	—	16.5	12.0	12.0
1.0	5.0	4.75	4.2	4.2	4.0	3.8	17.5	13.0	11.75
1.5	—	—	—	—	—	—	17.0	14.0	12.0
2.0	4.5	5.1	4.0	4.0	3.75	3.5	17.5	14.5	12.5
2.5	—	—	—	—	—	—	17.5	14.8	12.5
3.0	5.0	4.75	4.5	4.0	3.5	3.5	17.7	14.5	13.0
3.5	—	—	—	—	—	—	18.2	15.0	13.0
4.0	5.0	5.0	4.25	3.9	3.75	3.5	18.2	15.0	13.5
4.5	—	—	—	—	—	—	18.0	15.0	13.0
5.0	5.5	5.1	4.75	4.0	4.36	3.4	19.2	15.0	13.5
Average cc. per minute	4.76			3.89			29.7		
Specific conductivity	61.0×10.0^{-4}			30.0×10^{-4}			76.0×10^{-4}		

TABLE III

VOLUME OF HYDROGEN EVOLVED BY BAR OF MAGNESIUM FROM

Time	Solution (A) cc	Solution (B) cc
0.5 min.	13.0	6.0
1.0	14.0	6.5
1.5	14.0	6.25
2.0	14.5	6.5
2.5	14.5	6.5
3.0	15.0	—
3.5	15.5	11.75
4.0	15.5	—
4.5	15.5	11.75

The total volumes of hydrogen are 131.5 cc from solution (A) and 55.2 cc from solution (B), the ratio being 2.38 to 1.

The electrical conductivity of solution (A) was 931×10^{-6}, and that of solution (B) was 158×10^{-6}, the ratio being 5.9 to 1. If the conductivity is any measure of the number of ions, which are supposed to produce the chemical activity, it is difficult to see how the activity of the liquid can increase so much faster than the conductivity.

(4) Another experiment of this sort will be described. Solution (A) containing 50 cc of glacial acetic acid and 50 cc of water, and its conductivity at 7.5° C was 69×10^{-5}. Solution (B) consisted of 4 cc of 5N hydrochloric acid, 76 cc of acetone, and 22.5 cc of benzol. Its conductivity was 70×10^{-5}.

TABLE IV

VOLUME OF HYDROGEN EVOLVED BY BAR OF MAGNESIUM FROM

Time	Solution (A) cc	Solution (B) cc
30 seconds	10.75	—
60	12.25	6.0
90	12.25	—
120	12.5	6.1
150	11.0	—
180	13.75	5.75
210	12.5	—
240	13.0	5.9
270	13.0	—
300	13.0	6.2
	124.0	29.95

The ratio of the rates of hydrogen evolution is 4.1 to 1.0, whereas the conductivity of the solutions is practically identical.

(5) A solution of 10 cc lactic acid, 65 cc of water, and 42 cc of acetone was observed to evolve hydrogen at the rate of 1.4 cc per minute, when the bar of magnesium was dropped into it. The conductivity of the solution was 71×10^{-5} at 25° C. Another solution containing 3.33 cc of the same lactic acid, 60.67 cc of water, and 30 cc of acetone, evolved hydrogen at the rate of 1.07 cc per minute, and its conductivity was 74×10^{-5} at 25° C. Here the activity is increased and the

conductivity is diminished at the same time and by the same means.

In all of these experiments, it was carefully noted that the metal at no time became coated with anything like a scale or crust during the action of the acids upon it. On the contrary, it shone with a silvery lustre undimmed at any time. The products of the action were in every case completely soluble in the liquids. The gas evolved did not adhere to the metal, but escaped rapidly from its surface. The solution, being continually shaken, remained uniform in composition and the rate of action was not affected by the accumulation of the products in any one portion of the solution.

(6) Another favorite method of determining the activity of acids is to observe the rate at which they cause the catalytic decomposition of esters. Ostwald has recorded experiments showing how the addition of acetone to a nitric acid solution affects the rate at which it decomposes methyl acetate. He did not, however, record any conductivity measurements on these solutions. The following table is copied from his published results.[1] In each of the six mixtures there was present 5 cc 2N nitric acid, 2 cc methyl acetate, and other substances as indicated below.

TABLE V

Solution No.	Solvent	Ester decomposed in four hours
(1)	8 cc water, 0 cc acetone	23.14 cc standard baryta
(2)	7 cc " 1 cc "	21.91 cc "
(3)	6 cc " 2 cc "	21.56 cc "
(4)	4 cc " 4 cc "	17.83 cc "
(5)	2 cc " 6 cc "	15.11 cc "
(6)	0 cc " 8 cc "	12.00 cc "

For the purpose of this study, solutions were prepared having exactly the same composition as those listed above and their conductivity was determined, the results being as follows:

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[1] Jour. prakt. Chem. 136, 460 (1883).

TABLE VI

Solution No.	Specific conductivity
(1)	26.5×10^{-2}
(2)	25.6×10^{-2}
(3)	25.2×10^{-2}
(4)	19.5×10^{-2}
(5)	13.6×10^{-2}
(6)	8.1×10^{-2}

It is clear that by the use of acetone the electrical conductivity is diminished about 1.7 times faster than the chemical activity with respect to the catalysis of the ester.

(7) The preceding experiments have served to indicate that by the use of suitable solvents the electrical conductivity of a solution can be varied very greatly without at the same time effecting a corresponding change in the chemical activity. To test this view still further, the following experiment was performed. Three solutions were prepared.

TABLE VII

Solution (A)	Solution (B)	Solution (C)
5 cc 5N HCl	5 cc 5N HCl	5 cc 5N HCl
60 cc water	12.5 cc acetone	—
—	47.5 cc benzol	60 cc acetone

The specific conductivity of these solutions was respectively, 39000×10^{-5}, 171×10^{-5}, 365×10^{-5}.

After adding 10 cc of methyl acetate to each, the conductivity was 26480×10^{-5}, 215×10^{-5}, 312×10^{-5}.

The rate at which the ester was decomposed was determined by titrating portions of the liquids with standard baryta solution, at intervals, as indicated in the table.

Comparing the aqueous acid (A) with the acetone acid (C), it is clear that the former conducts about 107 times as well as the latter, but decomposes methyl acetate only about 1.6 times faster. Similarly, solution (A) has about 228 times the conductivity of (B), yet it decomposes methyl acetate

Time Minutes	cc	Time Minutes	cc	Time Minutes	cc
10	2.3	7	1.25	8	1.8
16	2.7	12	1.85	15	2.1
58	4.35	22	2.10	63	3.25
142	7.50	93	3.60	144	5.85
206	9.60	198	6.10	206	6.75
274	11.60	265	6.80	277	7.80
324	13.00	324	7.65	326	8.15
357	13.75	376	8.10	374	8.55
		444	8.75		

only about 2.6 times as fast as (B). It is evident that here no interdependence exists between the conductivity of these acids and the rate at which they decompose the ester, and it is equally certain that by the selection of suitable solvents the conductivity can be varied at will and practically independently of the activity. The following table contains a summary of the preceding experiments.

Table VIII

Experiment	Rate of activities	Rate of conductivities
(1) Sugar inversion	1 : 1	1 : 4.8
(2) 68 percent acids-magnesium	1 : 1.2	1 : 2.0
(3) 68, 34 percent acids-magnesium	1 : 6.25	1 : 1.25
(4) Acetic acid, HCl, and magnesium	1 : 4.1	1 : 1
(5) Lactic acid and magnesium	1 : 1.31	1 : 0.96
(6) Methyl acetate and nitric acid	1 : 1.92	1 : 3.27
(7) Methyl acetate and hydrochloric acid	1 : 6.0	1 : 107
(8) Methyl acetate and hydrochloric acid	1 : 7	1 : 228

It may be noted here that in 1, 2, 6, 7, 8, above, the conductivities change more rapidly than the rate of chemical activity, while in 3 and 4, the activity changes more rapidly than the conductivity. In 5, is found a case of simultaneous decrease of conductivity and increase of activity. There would be no difficulty in multiplying such cases *ad libitum.* The discussion of these results will be undertaken later.

Chemical Activity in Non-Conducting Solutions

Previous studies at this University have shown that certain chemical reactions do take place with ease in non-conducting solutions. Kahlenberg[1] has shown that the oleate of cobalt dissolves in toluene to a red solution which turns blue on heating, and red again on cooling. Zinc is attacked by a benzene solution of hydrochloric acid gas. Tin, aluminum, lead and sodium also react like zinc but less vigorously. The solution of hydrogen chloride in benzene precipitates brown cupric chloride from copper oleate solution, brownish yellow nickel chloride from nickel oleate solution, and blue cobalt chloride from cobalt oleate solution in benzene. Tin tetrachloride, phosphorus trichloride, arsenic chloride, and silicon tetrachloride behave like hydrochloric acid in precipitating these insoluble chlorides from the non-conducting solutions. Dry hydrogen sulphide passed into the benzene solutions of the oleates of copper, nickel, or cobalt or the chlorides of tin or arsenic precipitates the sulphides of these metals. In benzene solution, dry ammonia and dry hydrogen chloride combine and precipitate solid ammonium chloride. Dry pyridine in benzene solution forms with dry hydrogen chloride the white crystalline pyridine hydrochloride at once. None of the above-mentioned solutions conduct the current. Working in this laboratory, J. H. Mathews[2] found that trichloracetic acid dissolves in ethyl silicate to a solution having a specific conductivity less than 3×10^{-8}, which attacks magnesium rapidly with evolution of hydrogen. A saturated solution of trichloracetic acid in nitrobenzene exhibits a specific conductivity of $\cdot 1.46 \times 10^{-5}$ and acts upon zinc, nickel, magnesium, cobalt, cadmium, copper, bismuth, iron and sodium with various degrees of vigor. Trichloracetic acid in benzene acts on the metals vigorously but its conductivity is less than 3.8×10^{-8}. The same result is obtained with a kerosene solution of trichloracetic acid.

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[1] Jour. Phys. Chem., 6, 6 (1902).

[2] Ibid., 9, 641 (1905).

Magnesium acts upon the non-conducting solutions of crotonic, trichlorlactic, glacial acetic and dichloracetic acids. A 41 percent solution of cyanogen iodide in allyl mustard oil shows a conductivity of 1.36×10^{-8} and attacks magnesium, sodium and zinc. Kahlenberg[1] observed that normal solutions of trichloracetic acid in methyl, ethyl, or amyl sulphocyanates or in ethyl or allyl mustard oils rapidly attack magnesium and the dry carbonates of sodium and potassium, while the solutions are excellent insulators. Kahlenberg and Schlundt[2] have observed that liquid hydrocyanic acid, whose specific conductivity was 0.4×10^{-5}, attacks sodium and potassium, but fails to attack other metals or carbonates. Solutions of hydrogen chloride and other acids in liquid hydrocyanic acid conduct much better, but fail to attack various metals and carbonates.

Continuing this line of work under Professor Kahlenberg's direction, I have found that the precipitation of one metal by another from a salt solution takes place in non-conducting solutions also. For the purpose of these experiments, solvents were selected which do not themselves conduct the current, such as benzol, kerosene, pyridine and a great variety of other organic liquids. The ordinary salts of the metals, as the chlorides, acetates, sulphates, or nitrates, are quite insoluble in most of these liquids; but certain of the salts of organic acids, as the oleates and palmitates, are easily soluble in many of them. In general, these solutions conduct no better than the solvents themselves. Where the solvent is observed to show some slight conductivity of its own, the addition of copper oleate or other soluble copper salt to the liquid is quite as likely to decrease as to increase the conductivity. For example, a sample of amyl nitrite from Schuchardt showed a conductivity of 1.5×10^{-6}, and after dissolving a few percents of copper oleate in it, the conductivity was found to be 1.1×10^{-6}. The conductivity of a specimen of turpentine which had been dried by calcium chloride was

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[1] Zeit. phys. Chem., 46, 63 (1903).

[2] Jour. Phys. Chem., 6, 447 (1902).

found to be less than 1.6×10^{-8}, and after dissolving some copper oleate in it, the conductivity was found to be practically unchanged. It was next sought to determine whether such solutions as these act chemically upon the metals. Only a small portion of this field could be explored even in a qualitative way, as the total number of possible reactions is very great.

Action of Metals on Copper Oleate Solutions

A solution of copper oleate in amyl nitrate was found to have a conductivity of 2.6×10^{-7}, the same as the pure solvent. This was placed in a flask with pieces of copper, silver, bismuth, cadmium, antimony, magnesium, cobalt, aluminum, tin, iron, lead and solder, connected to a reflux condenser, carrying a calcium chloride tube at its upper end, and heated in a boiling water bath for two hours. The lead and cadmium were found to be coated with bright red metallic copper, the bismuth was tarnished somewhat and all the rest of the metals were unaffected. The metals used in these tests were of the best quality obtainable, and were all scraped bright with a steel tool before use, each time. The copper oleate was pure and anhydrous, as was also the amyl nitrate.

A solution of copper oleate in kerosene was heated 3.5 hours to 100° C with zinc, solder, lead, silver, cobalt, nickel, copper, bismuth, antimony, magnesium, tin, platinum, cadmium and iron. The zinc, cadmium and lead were found to be coated with metallic copper, and the other metals were unaffected. The lead acted most rapidly. Sodium was not affected by heating to 100° C under the solution of copper oleate in kerosene.

Using carbon bisulphide as a solvent for the copper oleate, magnesium, platinum, iron, antimony, bismuth, cobalt, nickel, solder, silver, tin and lead were all unaffected by heating the solution to boiling for four hours. No copper was deposited in any case. In a sealed tube, the carbon bisulphide solution was heated with zinc, aluminum, cadmium, silver, magnesium, tin, cobalt, nickel, iron, antimony, bismuth, manganese, lead, and solder to 100° C for two hours, and then left in the cold thirty-six hours longer. The silver was observed to be blackened. The solution was still blue, and no red metallic copper was deposited in any case.

A solution of copper oleate in ethyl acetate, dried by calcium chloride, was heated to boiling for three hours with bismuth and cadmium which were slightly tarnished thereby, and with iron, tin, silver, zinc, solder, magnesium, antimony and aluminum which were not changed. Metallic lead was not affected by boiling five minutes in this solution. The conductivity of the solution was less than 1.6×10^{-8}.

In dry acetone solution of copper oleate, heated to boiling for three hours, magnesium, cadmium, tin, platinum, nickel, copper, zinc, aluminum, antimony, bismuth and iron remained unchanged. The conductivity of the solution was 2.6×10^{-5}.

In a sealed tube, a solution of copper oleate in carbon tetrachloride was heated to 100° C for two hours. The zinc and lead had each a little dark red powdery deposit on them, and the other metals remained perfectly bright and unattacked.

In benzylamine solution of copper oleate, heated to 100° C for four hours, zinc and cadmium were coated with a slight pulverulent deposit, lead received a bright red deposit of metallic copper, while silver, magnesium, bismuth, antimony, zinc, cadmium, tin, nickel, cobalt, platinum, iron and aluminum remained perfectly bright and unchanged.

A solution of copper oleate in pyridine was heated to its boiling-point for two hours in a paraffin bath with zinc, cadmium, silver, lead, magnesium, platinum, iron, bismuth, antimony, tin, solder, nickel, and cobalt. The lead and cadmium were found to be coated with copper and the zinc was tarnished. The other metals were unchanged. Thallium was tarnished in the same liquid on warming. The pyridine used was of "medicinal" purity from Merck. It was dried with caustic potash and redistilled before use. It boiled at 113.5–116.5° C, uncorrected. The conductivity of the pyridine was less than 1.6×10^{-8}.

Replacement of Copper by Lead in Non-Conducting Solution

After digesting a solution of copper oleate in pyridine in a flask with a strip of lead for two hours at the boiling-point, under the reflux condenser, the liquid was of a brown color and no green or blue was visible. The lead was thickly coated with a layer of coherent copper, bright red, and lustrous, which flaked off in large pieces on rubbing. It was washed in alcohol and ether and preserved. The liquid was filtered and evaporated to free it from pyridine, the residue was dissolved in alcohol and dilute nitric acid, heated and treated with hydrogen sulphide. The black precipitate of sulphide was filtered, washed, and dissolved in nitric acid, evaporated with C. P. sulphuric acid and diluted with alcohol. The heavy white precipitate of lead sulphate obtained was washed, dried, and preserved. On evaporating the filtrate to small bulk, and adding ammonia, a faint blue color showed the presence of a small amount of copper in the solution. It is hereby shown that lead actually dissolves at the same time the copper is precipitated, and that the reaction which takes place when lead acts on a copper oleate solution in pyridine may be expressed by the equation

$$(C_{18}H_{33}O_2)_2Cu + Pb = (C_{18}H_{33}O_2)_2Pb + Cu.$$

Influence of Water on Action of Lead on Copper Oleate

In order to see what influence the presence of small proportions of water would have, portions of the copper oleate pyridine solution were heated in test-tubes with various metals to 100° C, then 10 percent water was added slowly, continuing the heating. In the tubes containing iron, tin, antimony, bismuth, cobalt, aluminum and silver no change whatever occurred on adding water. In the tubes containing magnesium, cadmium, and zinc, the addition of water caused a distinct red metallic deposit of copper. In the tube containing calcium both hydrogen and copper were deposited on adding water.

Using toluene as the solvent for the copper oleate, it was observed that lead precipitates metallic copper upon standing a few hours in the cold, or at once, if the solution be heated, while magnesium, zinc, silver, bismuth, tin, solder, cadmium, iron, antimony, cobalt, nickel, platinum, manganese, mercury, aluminum are unaffected in any way at 100° C in six hours. Sodium melted under the toluene solution of copper oleate is not changed. The conductivity of the solution is less than 1.8×10^{-8}. The oleates of cadmium, magnesium, zinc, manganese, nickel, iron and cobalt are all easily and completely soluble in toluene. Some of the toluene was treated with phosphorus pentoxide in a distilling flask, and after several days was distilled into a dry flask containing metallic lead and dry copper oleate. The apparatus was put together air-tight, and the flask was protected by a calcium chloride tube passing through the cork. Without disconnecting the receiver, the distillate was gently warmed by a lamp, when the copper oleate dissolved rapidly, and the metallic copper precipitated abundantly at once. These experiments show that the presence or absence of water in small proportions does not determine the precipitation of copper by lead in these cases.[1] In order to see whether other oleates behave like copper oleate, the following experiments were performed.

Action of Metals upon Various Other Metallic Oleates

Small portions of the oleates of manganese, chromium, nickel, cobalt, iron, and cadmium, were dried at 150–175° C for two hours and cooled in a desiccator. The solution of the dried nickel oleate in toluene was boiled with pieces of metallic magnesium, cadmium, zinc, bismuth, antimony, lead, tin, cobalt, aluminum, silver, manganese, platinum, iron, solder and copper for two hours under a reflux condenser, provided with a calcium chloride tube at the upper end. None of these metals was affected, excepting lead, which was covered with a black scale.

Manganese oleate in toluene solution, was heated similarly

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[1] In this connection compare the work of J. H. Mathews upon the effect of small amounts of water. Jour. Phys. Chem., 9, 641 (1905).

with lead, magnesium, zinc, antimony, silver, cadmium, iron, cobalt, aluminum, bismuth, solder, nickel, and copper. The only metal affected in any way was lead, which was covered with a black scale.

Cobalt oleate solution in toluene was placed in a flask with metallic silver, magnesium, cobalt, antimony, lead, tin, zinc, manganese, bismuth, copper, cadmium, iron, platinum and nickel and heated to boiling for two hours. The only metals changed were lead which received a black deposit, and copper which was stained nearly white, with a metallic lustre.

Chromium oleate in toluene was heated with metallic silver, magnesium, cobalt, antimony, lead, tin, iron, zinc, nickel, cadmium, bismuth, copper and manganese; but as before, lead alone was affected and this was coated with a black scale.

Ferrous oleate in boiling toluene solution, for two hours, with bismuth, antimony, nickel, iron, zinc, cadmium, magnesium, tin, silver, aluminum, cobalt, copper, lead and manganese, did not affect any of these metals.

Cadmium oleate in boiling toluene solution, for two hours with cobalt, cadmium, bismuth, antimony, silver, copper, magnesium, lead, zinc, iron, tin, aluminum and nickel, deposited a fragile black scale on the lead, and all of the other metals were unaffected. The solution gelatinized on cooling.

The experiments described above indicate that the reaction of lead with the copper oleate solutions proceeds far more rapidly and easily than any of the others tried, and the study of this reaction was therefore taken up in greater detail. The black scales observed in a few cases above, which formed also on lead in a few copper solutions, as noted below, were always very small in amount. They were too thin and minute in quantity to separate from the lead for analysis; and consequently, they were not examined further than to test some of them for radioactivity, which property was, however, not observed in any case. The question now arose as to whether other salts of copper behave toward lead like the oleate.

Action of Metals on Copper Salts Other than the Oleate

Copper palmitate was prepared by adding to copper sulphate, in aqueous solution, an equivalent quantity of solution of potassium palmitate, which was prepared by treating pure palmitic acid with the requisite quantity of potassium hydroxide. The precipitate was washed free of sulphate by decantation, and dried at 100° C to a fine blue powder. The salt melts at higher temperatures without apparent decomposition. A toluene solution of this salt was heated to boiling for two hours with bismuth, magnesium, antimony, cobalt, silver, zinc, lead, tin and cadmium. The lead was thickly coated with black scale, the bismuth was tarnished, and the others were entirely unchanged.

Copper palmitate dissolved in pyridine deposits bright red metallic copper on lead at once on gently warming.

A sample of abietic acid prepared from Oregon balsam, furnished by Professor Kremers, was made into the copper salt, which was dried at 120° C. The boiling pyridine solution of this salt did not act on lead.

Capronic acid (ex butyric acid) was redistilled, boiling-point 196–199° C, and converted into the copper salt by neutralizing with caustic potash and then adding copper sulphate solution in molecular proportion. The copper capronate was washed by decantation till entirely free from sulphate, and dried in air to a fine blue powder. On heating up the blue salt to about 100–125° C, it suddenly turned green and remained green on cooling. The change in color took place suddenly and uniformly throughout the mass. Both the blue and green varieties dissolve easily in pyridine to a green solution. On heating this solution with lead, the liquid turns brown instantly, and deposits copper on the lead at once, from the fairly strong, hot solution, but not so quickly if the solution is more dilute.

Crystallized copper acetate, from Schuchardt, was found to dissolve in pyridine to a deep blue solution whose conductivity was 6.6×10^{-7}. The solution was quite dilute. Metallic lead gently warmed in this solution was quickly coated with a bright red precipitate.

Crystallized copper formate from Schuchardt, dissolved in pyridine to a deep blue solution, whose conductivity was 9.6×10^{-7}. This quite dilute solution heated with lead turned green and deposited copper on the lead at once.

It is thus perfectly clear that the action of lead on copper salts is not restricted to the oleate, since the capronate and palmitate act in the same way.

Action of Lead on Fused Copper Salts

To test the action of lead upon the copper salts in the absence of solvents, the salts were placed in test-tubes and heated in a paraffin bath which contained a thermometer and a stirrer. As soon as each salt melted, a piece of lead was dropped into it and the temperature was held constant for a few minutes. The lead was then withdrawn with its adhering layer of fused salt, and after cooling in air, was dipped into some carbon bisulphide, which rapidly dissolved off the copper salt and exposed the clear surface of the metal. Carbon bisulphide was used because it had already been shown that solutions of copper oleate in this solvent do not attack lead. By this method, it was found that fused oleate deposits copper on lead at 100° C in five minutes or less.

Copper palmitate has a higher melting-point. At 125–140° C, it was quite fluid and deposited copper on the lead easily.

Copper abietate at 185–195° C, did not deposit copper on lead. Clean lead pressed into copper oleate somewhat softened by warming was found to have precipitated no copper at all in twelve hours.

Do Solvents Aid or Hinder the Action of Lead on Copper Oleate?

In order to find out whether various solvents aid or prevent this reaction between lead and copper oleate, these solvents were first examined as to their conducting power, then the liquid in the conductivity vessel was poured out into a clean testtube, a fragment of copper oleate was added and the liquid warmed, but not above 110–115° C. If copper was deposited on the lead in the tube, the liquid was poured back into the conductivity cell, in order to determine the conductivity of the solution. In the following tables, the word "none" means that no conductivity could be detected by means of the telephone, Wheatstone's bridge, and 11000 ohms resistance, according to the method of Kohlrausch. In such cases, the conductivity, if any, is less than 1.6×10^{-8}. Lead precipitates copper from a solution of copper oleate in each solvent in the following list.

TABLE IX

Solvent	Spec. cond. of solvent	Spec. cond. of solution
Kerosene	None	None
Nonane (Ohio petroleum)	None	“
Petroleum (Japanese) B. P. 116–118	Not determined	—
“ “ “ 196–197	“ “	—
Amylene	“ “	—
Dipentene (S)	“ “	—
Paraffin, melted	“ “	—
Diphenylmethane (K)	“ “	—
Triphenylmethane, melted (K)	“ “	—
Toluene (S)	None	None
Xylol	Not determined	—
Spermaceti, melted (E)	“ “	—
Limonene	None	None
Retene, melted (S)	Not determined	—
Turpentine	None	None
Cymene (*e*-camphora)	Not determined	—
Terpinene	None	None
Mesitylene	Not determined	—
Naphthalene, melted	“ “	—
Anthracene, melted (M)	“ “	—
Alcohols and Phenols		
Ethyl, by CaO (S)	2.2×10^{-6}	9.0×10^{-6}
Isopropyl (S)	3.3×10^{-6}	5.6×10^{-6}
Normal propyl (S)	7.4×10^{-7}	1.5×10^{-6}
Allyl	Not determined	—
Isobutyl	3.4×10^{-7}	None
Isoamyl (K)	5.1×10^{-7}	5.1×10^{-7}
Cumol	—	—
Guaiacol (Merck)	2.6×10^{-7}	2.0×10^{-7}
Eugenol (S)	None	None
Phenetol (S)	“	“

TABLE IX—(*Continued*)

Solvent	Spec. cond. of solvent	Spec. cond. of solution
Alcohols and Phenols		
Phenol, white, melted (K)	None	4.7×10^{-7}
Thymol, melted (S)	Not determined	—
Meta-kresol (S)	None	None
Ortho-kresol methyl ether (S)	"	"
Terpineol (S)	"	"
Carvacrol	Not determined	—
Amines, etc.		
Pyridine	None	None
Dibenzylamine	"	"
Benzylamine	"	"
Aniline	"	0.2×10^{-7}
Picoline (S)	5.3×10^{-7}	8.1×10^{-7}
Ortho-toluidine (M)	1.7×10^{-6}	1.7×10^{-7}
Quinoline, synthetic, redistilled (S)	None	None
Urethane, melted (S)	Not determined	"
Pyrrol	" "	"
Ethereal Salts, etc.		
Ethyl oxalate	1.1×10^{-6}	9.6×10^{-7}
Ethyl carbonate	None	None
Ethyl nitrate	2.0×10^{-6}	6.7×10^{-7}
Amyl nitrate (S)	2.6×10^{-7}	2.6×10^{-7}
Amyl nitrite (S)	1.5×10^{-6}	1.1×10^{-6}
Amyl benzoate (S)	None	None
Amyl acetate	Not determined	—
Aceto-acetic ester (S)	1.7×10^{-6}	Not determined
Monochlorhydrin (S)	4.9×10^{-7}	8.7×10^{-6}
Dichlorhydrin (S)	1.09×10^{-5}	7.38×10^{-6}
Cottonseed oil, refined	Not determined	—
Brombenzene	None	None
Benzyl aceto-acetate (S)	Not determined	—
Nitriles, etc.		
Capro-nitrile	3.3×10^{-6}	3.2×10^{-6}
Valero-nitrile (S)	5.4×10^{-6}	4.2×10^{-5}
Benzo-nitrile	9.9×10^{-6}	3.1×10^{-6}
Toluo-nitrile	5.4×10^{-6}	4.2×10^{-5}
Nitrobenzene (K)	4.0×10^{-7}	4.0×10^{-7}
Aldehydes, ketones, etc.		
Acetyl-acetone (S)	3.6×10^{-6}	4.2×10^{-6}
Acetyl methyl hexyl ketone (S)	None	None
Acetophenone	1.6×10^{-6}	2.2×10^{-6}
Anisic aldehyde (S)	1.7×10^{-6}	1.7×10^{-6}
Benzaldehyde (not free of acid)	Not determined	—
Menthone	None	None

Solutions of copper oleate in the following solvents gave no deposit of copper on lead, even after heating above the boiling-point of the solvent in a sealed tube. The solutions were, however, quite dilute and it is possible that stronger solutions might act in some cases.

TABLE X

Solvent	Spec. cond. of solvent	Spec. cond. of solution
Acetone	2.6×10^{-5}	Not determined
Methyl sulphate	1.9×10^{-4}	2.0×10^{-4}
Methyl iodide (K)	1.3×10^{-7}	None
Ethyl acetate	None	"
Ethylidene chloride (S)	"	1.3×10^{-7}
Pentane (S)	Not determined	—
Hexane (S)	" "	—
Ligroin	" "	—
Rhigolene	" "	—
Benzol, thiophene-free	" "	—
Furfurol (S)	6.8×10^{-6}	7.8×10^{-6}
Carbon bisulphide	Not determined	—
Carbon tetrachloride	"	—
Piperidine (S)	"	—

The letters in parentheses (S), (K), (M), (E) indicate the source of the substance, Schuchardt, Kahlbaum, Merck, Eimer and Amend. All of the copper oleate used was dried in an air-bath at 130°–140° C in thin layers before use and was afterward cooled over sulphuric acid in a desiccator and preserved in stoppered weighing-tubes. The other copper salts were similarly dried and none of them show any indication of being hygroscopic. The solvents were anhydrous and of the best grade, and some of them were especially dried with great care.

The experiments already described show that the solvent, the metal, the acid radical in the copper salt, and the temperature are all important factors in determining whether reaction occurs or not. It was observed also that stronger solutions of copper oleate in pyridine or toluene act more rapidly on lead than dilute solutions, and this fact led to an attempt to compare these rates of action. A preliminary experiment was begun in which the rates of deposition of copper from solutions of different concentration were to be estimated from the rate at which the blue color disappeared from the liquids. The colorimetric measurements were, however, not performed, on account of the appearance of new and unforeseen phenomena, to be described below.

Effect of Concentration on the Precipitation of Copper by Lead from Copper Oleate Solutions

Two grams of copper oleate were weighed in a flask and 38 grams of pyridine were added, making a 5 percent solution of the salt. This was placed in a burette and diluted in test-tubes with pyridine from another burette, as follows, thus preparing solutions with approximately the percentage composition indicated.

n cc 5 percent sol. of copper oleate + *m* cc pyridine gave approximately a solution of *p* percent copper oleate.

	n cc	*m* cc	*p* Percent
(1)	1.9	0.1	4.75
(2)	1.8	0.2	4.50
(3)	1.7	0.3	4.25
(4)	1.6	0.4	4.00
(5)	1.5	0.5	3.75
(6)	1.4	0.6	3.50
(7)	1.3	0.7	3.25
(8)	1.2	0.8	3.00

After standing corked for four hours at room temperature, about 23° C, the lower half of each piece of lead in solutions 1 to 6 was found to be coated with metallic copper, bright and coherent, and the lower half of the liquid in these tubes was no longer blue, but colorless or slightly yellow. After standing a little longer, the entire liquid in these tubes was decolorized and the entire lead surface was coated with copper. In solutions 7 and 8, not the slightest change in the appearance of the solutions or of the lead could be detected after four hours, nor indeed at any subsequent period. After thirty days, there was still no visible change in the blue copper solutions nor was any copper deposited on the lead. The lead, however, had not so bright a lustre as when put into the liquid and might have been corroded somewhat. A similar experiment was performed, in which the solutions containing the metallic strips were kept in a boiling water-bath. A 1 percent solution of copper oleate in pyridine did not deposit any trace of copper on lead inside of two hours, while 2 percent and 4 percent solutions deposited a bright coherent coating of copper on the lead within two minutes, that is, as soon as they got warm. In a similar way, it was found that within four hours, at 23° C, a bright deposit of coherent metallic copper is formed on metallic cadmium placed in pyridine solutions containing 25 to 2.75 percent of copper oleate, but not at all in 2.5 percent or weaker solutions. At 100° C, a 1.7 percent solution will deposit copper on cadmium, but a 1 percent solution will not. At room temperature, in three hours, metallic zinc completely decolorizes a pyridine solution containing 2.1 percent of copper oleate, the zinc being coated with copper at the same time. A 2.0 percent solution, however, undergoes no change in color even after several weeks' standing, nor is any copper deposited on the zinc.

In view of these facts, which were found out in the latter part of this investigation, the deposition of copper might occur in some of the solvents listed in Table X, if very concentrated solutions of copper oleate were used. To test this in a single case, a solution containing 36 percent of copper oleate in carbon bisulphide was warmed to its boiling-point with lead for several minutes, and allowed to stand in the cold for several hours. The lead was stained black in some places, but no red metallic copper was deposited.

The fact that a 2.1 percent copper oleate solution is decolorized by zinc in three hours, while a 2 percent solution does not react, does not seem to have any parallel among the reactions which occur in aqueous solutions. According to some of the prevalent notions, it would be expected that the more dilute the solution, the quicker it would be decolorized. On the contrary, the copper, in fact, is held more tightly bound in the weaker solution, so that the lead is not able to replace it at all.

Although the 2.5 percent solution of copper oleate in pyridine does not react with lead at all at room temperature, it can be made to react by adding 0.25 percent more of the copper salt. From this, it appears that the strength with which the solute is held is some inverse function of the quantity in solution. The question at once arose as to whether the addition of any other substance to the 2.5 percent solution of copper oleate would so loosen the hold of the solvent on the copper as to permit the reaction to proceed, as if a larger percentage of copper oleate were present.

To determine this, a 2.5 percent solution of copper oleate in pyridine was prepared and placed in testtubes. To one of them a piece of lead alone was added, but no reaction occurred within two days. To another, some cadmium oleate was added, and in one hour a heavy deposit of bright red copper had formed on the lead. In another portion, some refined glycerine oleate (cotton seed oil) was added with lead, and here too, within an hour, a bright lustrous deposit of copper had formed. In still another portion, some lead oleate was added, with lead, and, as before, the copper deposit appeared within an hour. A considerable amount of lead oleate must be added, as the addition of traces only was found to be ineffective in provoking action. According to the mass law, the addition of lead oleate to the solution should tend to hinder the further solution of metallic lead as oleate in the liquid, but quite the contrary is observed to be the case.

The fact that the presence of lead oleate in the solution accelerates the deposition of copper, as shown in this experiment, explains why a copper oleate solution is decolorized at the bottom first by lead, while the copper deposits more rapidly on the bottom end of the lead strip than at the top. As fast as lead oleate is formed by the reaction on the surface of the metal, it runs down to the bottom of the vessel, and collects there, and on account of its presence, the lower layer of the liquid more quickly deposits its copper. The decolorization of the liquid proceeds steadily up the tube as far as the top of the lead strip and then stops. This acceleration effect, due to loosening the hold between the solute and solvent, so far surpasses the retardation, by mass action of the lead oleate added, that the latter effect is masked.

Activity of Pure Lead and of Various Alloys

In the experiments recorded above, the lead used was from a lot labeled "test lead, free from silver" from Eimer & Amend. It was melted, cast into bars, and rolled out into thin ribbons, which were cut up, and freshly scraped with a steel tool just before use in each experiment. The attempt to use, instead of this, some ordinary commercial lead, after rolling and scraping, revealed the fact, at once, that the latter material would not precipitate copper from a 5 percent copper oleate solution in pyridine. This inactivity was attributed to the impurity of the lead.

The preparation of specially pure lead by the method of Stas[1] was next undertaken, in order to compare its activity with that of the test lead mentioned above. 365 grams of lead acetate dissolved in 1.5 litres of water, were digested for 100 hours at 40°–50° C, with several strips of pure lead foil. The liquid was filtered and run into a slight excess of a 10 percent solution of pure sulphuric acid. The precipitated lead sulphate was washed by decantation, and digested with an ammoniacal solution of ammonium carbonate in excess. The lead carbonate thus formed was washed thoroughly, drained, dried, and fused with potassium cyanide in a Hessian crucible. The button of lead obtained was remelted, cast into bars, and rolled out for use. This chemically pure lead was found to act upon the 5 percent copper oleate-pyridine solution, but not upon the 2.5 percent solution, precisely as the test lead from Eimer & Amend had done.

A number of experiments were performed to show whether the alloying of various quantities of foreign metals with the

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[1] Bull. Acad. roy. Belg., 10, 295.

lead would affect its activity. For this purpose, 1 percent of tin was added to pure lead, and this alloy, boiled with copper oleate in toluene, precipitated metallic copper, but not so rapidly as pure lead. A 2 percent tin alloy with lead acted more slowly with the same solution. With 3 percent of tin, the alloy showed slight traces of copper on its surface, after ten minutes' boiling of the solution. With 5 percent of tin, the metal is slightly blackened after long boiling, but no red copper deposit was obtained.

The addition of 1 percent cadmium to pure lead entirely stopped its action on a dilute solution of copper oleate in toluene. A 5 percent cadmium alloy behaved in the same way.

Alloys of lead with 4.3, 10.5 and 25.1 percent zinc, respectively, precipitate copper easily in bright red lustrous condition.

A 3.7 percent silver alloy with lead was soon coated with copper in the toluene solution. A 10 percent silver alloy precipitates copper more slowly, but the deposit was bright pink in color, and tightly adhering. A 42 percent silver lead alloy was tarnished somewhat.

The addition of 4.2 percent bismuth to pure lead forms an alloy which precipitates copper, lustrous and coherent, from the hot toluene solution of copper oleate. An 8.4 percent bismuth alloy received only a brownish yellow stain.

A 7.4 percent magnesium lead alloy precipitates copper easily and quickly from the hot toluene solution. Alloys containing 10.3 percent and 14.8 percent of magnesium, respectively, do not act on the solution. These latter alloys rapidly decompose hot water, evolving hydrogen gas and disintegrating. On exposure to air for a short time, they crumble to a black brittle powder.

On heating lead and bright metallic copper together for some time in a porcelain crucible, the corners of the copper strip were found to be rounded off, showing that some of the copper had alloyed with the lead. This lead copper alloy precipitates copper on its surface from the toluene copper oleate solution, but more slowly than pure lead.

Various alloys of lead and antimony containing from 37.4 to 1.2 percent of the latter metal were all found to have no action on the toluene solution of copper oleate.

The presence of 67 percent gold in lead alloy entirely prevents its action on the toluene solution of copper oleate. A 53 percent gold alloy with lead was very slightly tarnished, while a 0.53 percent gold lead alloy slowly took a reddish tinge on heating in the toluene solution of copper oleate, and an 0.18 percent gold lead alloy took a brass color on heating in the same solution.

A 27.7 percent mercury alloy with lead, does not act on a toluene solution of copper oleate, but in a pyridine solution of either copper oleate or copper palmitate it is soon covered with a dull gray pulverulent coating. Pyridine alone has no action on the alloy.

A 20 percent alloy of sodium or potassium with melted lead prepared by melting the metals together under paraffin, received only a slight black tarnish on heating it in the toluene solution of copper oleate. Some alloys of zinc and silver, zinc and magnesium, zinc and copper were tried, but they did not precipitate copper from the toluene solution of copper oleate.

From these experiments, it appears that the alloying of other metals with lead retards or prevents it from reacting with the copper solution, and that the kind of metal and the percentage of it present are important factors. To test this further, a small amount of an alloy of 5 percent tin and 95 percent lead was prepared, cast in a bar, rolled out into a thin ribbon, and cut up into slips 1 by 2 cm for use. 9.68 grams copper oleate and 24.78 grams pyridine were weighed in a flask, forming a 28.1 percent solution of the salt. Portions of this solution were diluted in testtubes with pure pyridine, so as to contain 2, 4, 10, 14, 20, 22, 24, 26 and 28 percent respectively, of the salt, and in each tube was placed a piece of the freshly scraped 5 percent tin alloy. All of the tubes were corked and set in a beaker of boiling water. As soon as the 26 and 28 percent solutions got hot (within two minutes), the bright red deposit of metallic copper appeared on the metal within. The other solutions were heated for two hours in the boiling water-bath, and although some of the metal slips were slightly tarnished or roughened, no deposit of copper was visible upon them at any time. Here, the very definite strength with which the copper is bound to the solution is clearly shown. The lead similarly is held in its alloy with a definite tenacity. When the concentration of the solution and of the lead in the alloy are adjusted to each other, so that the chemical affinities are in the proper relation, then reaction can occur and not otherwise.

In the experiments already described, it has been shown that the variable factors which aid or prevent chemical action are the temperature, the composition of the solvent, the composition of the metallic salt as to metal and acid radical present, the percentage strength of the salt in the solution, and the percentage composition of the metal or metallic alloy employed for precipitation.

Since the precipitation of copper by lead has been described almost exclusively, another example of this class of reaction was sought in order to see if the case of copper and lead is altogether singular and exceptional.

Precipitation of Mercury by Aluminum from Non-Conducting Solution

Mercury ethyl chloride, HgC_2H_5Cl, dissolves easily in benzol and the conductivity is less than 1.6×10^{-8}, cold or hot. This solution, warmed with metallic aluminum, magnesium, iron, copper, bismuth, antimony and platinum reacts with the aluminum only. Aluminum, alone, reacts easily and a gas is evolved, perhaps butane, the bubbles of which dissolve in the solvent before reaching the surface. The aluminum is rapidly amalgamated, and on removing it from the solution, it is found to have lost its lustre and to be deeply corroded. Dropped into water, the amalgamated metal reacts at once, evolving hydrogen gas copiously. The precipitation of one metal by another, is therefore, a general reaction, occurring in non-conducting solutions as well as in those which conduct.

Summary

The facts and conclusions of the preceding pages may be summarized as follows:

(1) It was shown by the substitution of benzol for water in aqueous acid solutions, that the activity of acids in inverting sugar, catalyzing esters, and dissolving magnesium can be made to vary entirely independently of the electrolytic conductivity of the solutions.

(2) It has been demonstrated that the replacement of one metal by another metal takes place in molten salts or solutions which are the best of insulators as well as in liquids which are good electrolytes.

(3) In view of these facts and others previously recorded by Kahlenberg[1] it is concluded that the predictions of Arrhenius[2] and Ostwald,[3] to-day widely quoted in text-books,[4] to the effect that electrolytic conduction and chemical activity are proportional, possess no general applicability.

(4) The precipitation of copper from non-conducting liquids and solutions of the copper salts that were studied is accomplished far more readily by means of lead than by sodium, magnesium, iron and other metals commonly considered as more electro-positive than lead. This shows, again, that electrical relations are not always necessarily parallel with chemical affinities.

(5) All other things being equal, the acid radical in the copper salt determines whether the copper will be replaced by lead or not. The oleate, palmitate, and capronate of copper

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[1] See references given above.

[2] "Text-book of Electrochemistry," page 182 (1902); Bijhang till K. Svensk. Vet.-Ak. Hand. Bd. 8, 13–14 (1884).

[3] Jour. prakt. Chem. 138, 93 (1884).

[4] Nernst: "Theoretical Chemistry," page 519 (1904); Jones: "Theory of Electrolytic Dissociation," pp. 157, 158 (1900); Arnold: "Abriss der allgemeinen oder physikalischen Chemie," p. 103 (1903).

are salts from whose non-conducting solutions, lead precipitates copper easily.

(6) From pure, dry, copper oleate in the molten state, lead deposits copper readily at 100° C.

(7) It was found that from 69 non-conducting solutions of copper oleate, prepared by using as many different solvents, copper is easily precipitated by lead. On the other hand, it was also found that from 14 other non-conducting solutions of copper oleate, lead does not replace copper. This shows that solvents are not "indifferent" even in such cases as those investigated, but are more or less tightly united to the solutes.[1]

(8) It was observed that at a fixed temperature, in a given solvent, a certain definite percentage or more of copper oleate must be present, in order that copper might be precipitated by a given metal. This minimum percentage of copper oleate is different for different solvents, for different metals and for different temperatures. The fact that such a minimum percentage exists in the case of non-conducting solutions has apparently no parallel in the case of aqueous solutions. Again, the precipitation of copper by lead from the copper oleate solutions is greatly facilitated by the presence of oleate of lead, cotton-seed oil or oleate of cadmium, though the presence of mere traces of these substances will not produce such effect.

(9) It was found, in alloying lead with other metals, that widely different percentages of the several metals, are required to stop the action of lead on the copper oleate solution. This shows that the metal added does not act simply as a diluent of the lead, but that the two are really chemically combined, though such alloys are frequently spoken of as solid solutions, a name which commonly suggests the absence of all attraction of a chemical character.

(10) An alloy containing certain proportions of tin and lead reacts at once with a copper oleate solution of a certain definite concentration, and not with a weaker solution. This shows that the copper is held more tightly in the weaker

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[1] Compare Kahlenberg: Chem. Zeitung, 29, 81 (1905).

solution than in the stronger, and that the alloy and the solution also are not mere mixtures, but each the product of chemical union between the constituents.

(11) While a number of previous investigators have observed that chemical activity and electrolytic conductivity frequently run parallel to each other, the experiments recorded in this paper, nevertheless, show conclusively that, as a matter of fact, no constant relation exists between electrolytic conductivity and chemical activity; in other words, these do not stand to each other in the relation of cause and effect.

The facts established are readily comprehended when solutions are regarded as chemical unions of solvent and solute.

In conclusion, I wish most cordially to thank Professor Kahlenberg for suggesting to me the work described above, and for the pleasure and profit which the time spent in his laboratory has afforded me.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, June, 1906.