for the preparation of pure ammonium acetate, and the uncertainty as to the melting point of this salt has been cleared up.

2. Solvation and solubility in these systems, and in others of the same type for which data are available, have been found to be closely related, in accordance with the theories of Kendall.

3. Attention has been called to the basic properties of acetates in acetic acid solution, and to the similarity in function between ammonia and water in this solvent.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

SOLUTIONS OF SALTS IN PURE ACETIC ACID. III. ZINC ACETATE AND SODIUM ZINC ACETATE[1]

BY ARTHUR W. DAVIDSON AND WALTER H. MCALLISTER

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Introduction

The solubility of zinc acetate in acetic acid was found by Kendall and Adler[2] to be very small, the saturated solution at 130° containing only about 0.1 mole per cent. of zinc acetate; no further data are given by these authors. In the first article of this series,[3] mention was made of the fact that the solubility of zinc acetate is greatly increased by the presence of sodium acetate, and it was pointed out that this was analogous to the behavior of zinc hydroxide, in aqueous solutions, upon the addition of sodium hydroxide; no quantitative work, however, has been done previously upon the ternary system sodium acetate–zinc acetate–acetic acid. In the present investigation the solubility of zinc acetate in acetic acid over a range of temperatures has been measured, both in the absence of sodium acetate and in the presence of increasing concentrations of the latter solute. Comparison of the results of these measurements with data given in the literature for the corresponding aqueous system has established the analogy between the two cases upon a firmer basis, and has made possible its further development, as will be shown below.

Method

Preparation of Materials.—The acetic acid employed was prepared as described in the preceding paper of this series. The sodium acetate was prepared by recrystallizing a C. P. hydrate from water and dehydrating it at 150° for about a week. Zinc acetate, it was found, could not be dehydrated even at temperatures as low as 90° without slow partial decomposition to a basic salt. The pure salt was made by re-

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[1] The material presented in this paper is from part of a thesis submitted by Walter H. McAllister to the Graduate School of the University of Kansas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[2] Kendall and Adler, THIS JOURNAL, **43**, 1470 (1921).

[3] Davidson, *ibid.*, **50**, 1890 (1928).

crystallizing the hydrate from dilute acetic acid, heating to 85–90° for several days, and then moistening the slightly basic product with pure acetic acid and heating again to 85° for six hours. A sample of this product showed, upon analysis carried out as described below, 35.64% of zinc (calcd. for $Zn(C_2H_3O_2)_2$, 35.65%).

Binary System.—The method used for determining the solubility of zinc acetate in pure acetic acid was the same as that described for other acetates in the preceding paper. Because of the very small solubility, in this case, and the very minute amount of solid which separated on cooling, the determination of the equilibrium temperature was somewhat troublesome. Nevertheless, with a reasonable amount of care, the temperatures were found to be reproducible, and those given are believed to be correct to within 0.5°.

Ternary System.—In the study of the ternary system, acetic acid solutions were prepared containing exactly 1, 2.5, 5 and 7 mole per cent., respectively, of sodium acetate. To these solutions increasing amounts of zinc acetate were added, and the equilibrium temperatures were determined just as in the binary systems. These temperatures were then plotted as ordinates against the mole percentages of zinc acetate as abscissas to give a series of curves, each individual one of which should represent the solubility of zinc acetate in a solution having a fixed value of the ratio, number of moles of sodium acetate/number of moles of (sodium acetate + acetic acid). To save space this mole ratio will subsequently be referred to simply as R.

Methods of Analysis.—Samples of the solid phases present at equilibrium were obtained by crystallization from the solutions under suitable conditions, followed by filtration and drying on porous tile as in previous work. In these cases, however, it was found to be impracticable to determine the acetic acid by direct titration, no accurate end-point being obtainable in the presence of zinc ion.[4] Analysis of these compounds was therefore carried out by the following means. In the case of the binary system the weighed sample was dissolved in water and the zinc determined by potentiometric titration at 65° with fortieth molar potassium ferrocyanide solution containing 0.1% potassium ferricyanide; this determination was sufficient to fix the composition of the compound. In the ternary system, however, it was necessary to determine a second constituent also. The acetates in the weighed sample were changed to sulfates by treatment with concentrated sulfuric acid, followed by heating to drive off acetic acid and excess sulfuric acid. The residue of sulfates was weighed, dissolved in water and zinc determined by potentiometric titration as above. The weight of zinc acetate in the original sample could be calculated directly from this titration, that of sodium acetate from the amount of sodium sulfate found by difference in the mixed sulfates, and acetic acid by difference between the total weight of the sample and the combined weights of zinc and sodium acetates.

The data obtained are tabulated below, and are represented also in the accompanying diagrams. The concentration of zinc acetate in the solution is expressed throughout in mole percentage; T is the equilibrium temperature.

A. BINARY SYSTEM $Zn(C_2H_3O_2)_2$–$HC_2H_3O_2$

(a) Solid phase $Zn(C_2H_3O_2)_2$

$Zn(C_2H_3O_2)_2$, %	0.0050	0.0054	0.0085	0.0109
T	40.5	43	48	52
$Zn(C_2H_3O_2)_2$, %	0.0150	0.0231	0.0382	
T	56	62	72	

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[4] An approximate determination could be made by potentiometric titration with sodium hydroxide solution, using a saturated quinhydrone electrode, but preliminary experiments showed the end-point obtained to be unreliable.

The curve for this system is given in Fig. 1. Due to the extremely small solubility of zinc acetate at low temperatures, it was found to be practically impossible to determine equilibrium temperatures below 40°. Enough points were obtained at higher temperatures, however, to make it possible to continue the curve to the eutectic point, with some degree of confidence, by extrapolation. The solubility at 25° appears to be 0.0018 mole per cent.

For the same reason, the solid phase (a) could not be obtained in sufficient quantity to afford as accurate an analysis as might be desired. However, analysis of a sample weighing 0.0720 g. showed 36.53% of zinc (calcd. for $Zn(C_2H_3O_2)_2$, 35.65%). The compound, therefore, is evidently unsolvated $Zn(C_2H_3O_2)_2$.

B. TERNARY SYSTEM $NaC_2H_3O_2$–$Zn(C_2H_3O_2)_2$–$HC_2H_3O_2$

1. Mole Ratio R = 0.01. (a) Solid Phase $Zn(C_2H_3O_2)_2$

$Zn(C_2H_3O_2)_2$, %	0.323	0.376	0.417	0.463	0.487
T	35.5	65	73	78	82

2. Mole Ratio R = 0.025. (a) Solid Phase $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$

$Zn(C_2H_3O_2)_2$, %	0.445	0.495	0.588	0.646	0.764
T	26.1	26.3	26.1	27.0	28.0
$Zn(C_2H_3O_2)_2$, %	0.862		0.865		
T	27.8		28.0		

(b) Solid Phase $Zn(C_2H_3O_2)_2$

$Zn(C_2H_3O_2)_2$, %	0.895	0.919	1.028	1.123
T	30	36	72	82

3. Mole Ratio R = 0.05. (a) Solid Phase $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$

$Zn(C_2H_3O_2)_2$, %	0.251	0.442	0.487	0.594	0.625	0.666
T	25.0	29.2	29.1	31.7	32.5	33.5
$Zn(C_2H_3O_2)_2$, %	0.701	0.763	0.809	0.852	1.106	2.162
T	33.5	35.0	35.5	36.7	39.8	42.0

4. Mole Ratio R = 0.07. (a) Solid Phase $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$

$Zn(C_2H_3O_2)_2$, %	0.247	0.294	0.464	0.469	0.662
T	26.7	28.5	33.9	33.2	36.1
$Zn(C_2H_3O_2)_2$, %	0.903	1.030	1.318	1.927	
T	41.2	42.7	46.0	48.6	

The curves for this system are given in Fig. 1. It is immediately evident that these curves exhibit a marked change in slope with change in the solid phase in equilibrium with the solution. The solid phase 1 (a) could not be obtained in sufficient amount for analysis, but it seemed certain, from their similarity in appearance and behavior, that it was the same as solid phase 2 (b). Analyses of the latter gave a mean value of 35.45% of zinc, which showed that the compound was unsolvated $Zn(C_2H_3O_2)_2$. Again, it seemed probable from the similarity in their appearance and in the slope of the corresponding curves that solid phases 2 (a), 3 (a) and 4 (a) were identical. Analyses gave the following figures:

Solid phase	Mole % of $Zn(C_2H_3O_2)_2$	Mole % of $NaC_2H_3O_2$	Mole % of $HC_2H_3O_2$
2(a)	14.38	29.45	56.17
3(a)	14.37	29.84	55.79
4(a)	13.33	27.80	58.88
Calcd. for $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$	14.29	28.57	57.14

Considering the difficulties involved in freeing these solid phases completely from the mother liquor, their instability in moist air and the necessity of determining one of the constituents by difference, these figures, it is believed, establish satisfactorily that the substances are all identical

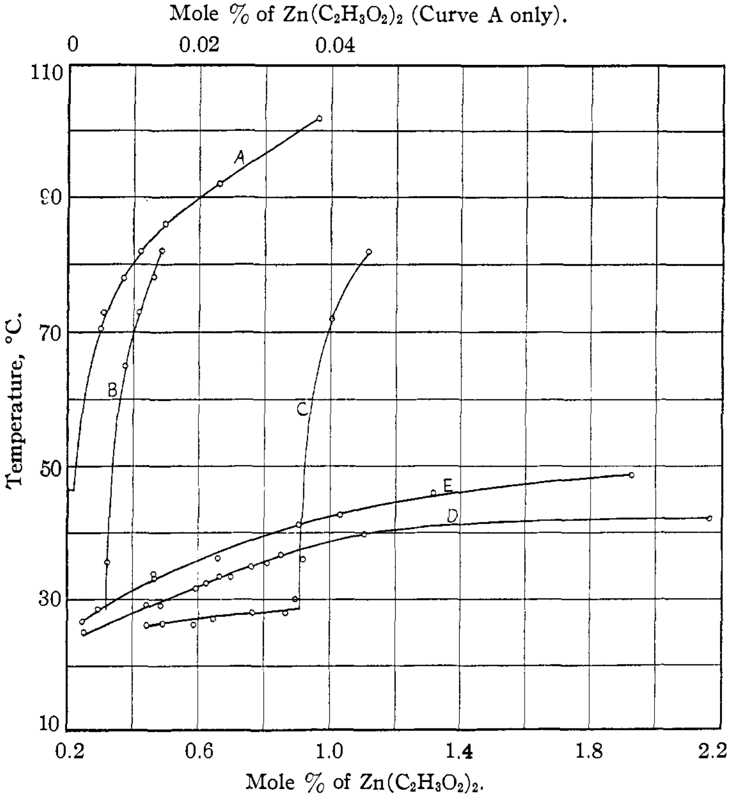

Fig. 1.—Solubility curves of $Zn(C_2H_3O_2)_2$ in pure $HC_2H_3O_2$ and in the presence of various concentrations of $NaC_2H_3O_2$. A, *R* = 0.00 (pure acetic acid); subtract 30° from temperature scale. B, *R* = 0.01; C, *R* = 0.025; D, *R* = 0.05; E, *R* = 0.07.

and consist of a ternary compound, or solvated sodium zinc acetate, of the composition given.

It now becomes apparent that the solubility of zinc acetate in acetic acid at a fixed temperature increases with increasing concentration of sodium acetate, so long as zinc acetate itself is the stable solid phase. Upon the appearance of the ternary compound, however, the mole percentage of zinc acetate in the saturated solution begins to decrease with increase in concentration of sodium acetate. This is brought out more clearly in Fig. 2, which shows an isotherm for 28.5°, plotted from data obtained from the curves in Fig. 1. Here the solubility of zinc acetate, which is only 0.0022 mole per cent. in pure acetic acid, increases upon the addition of sodium acetate until R is 0.025, where the solubility reaches a maximum of 0.91 mole per cent. At this point the solution can exist in equilibrium with both solid phases. Then with further addition of sodium acetate the mole percentage of zinc acetate in the saturated solution falls off, becoming 0.30 for $R = 0.07$. At slightly higher values of R, the compound $NaC_2H_3O_2 \cdot 2HC_2H_3O_2$ appears as solid phase. The investigation was not continued into this region.

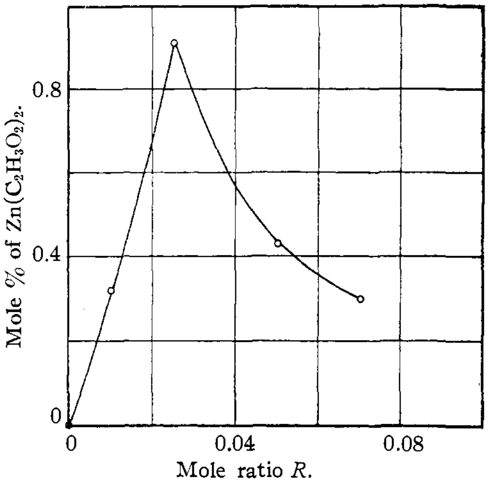

Fig. 2.—Effect of increasing concentrations of $NaC_2H_3O_2$ upon the solubility of $Zn(C_2H_3O_2)_2$ in $HC_2H_3O_2$ at a fixed temperature; isotherm at 28.5°.

Comparison of Results with Data for the Corresponding Aqueous System.—The system $Zn(OH)_2$–$NaOH$–H_2O has been studied quantitatively by a number of investigators.[5] Although the data of the various workers show rather poor agreement,[6] it has been observed in every case that the solubility of zinc hydroxide at a fixed temperature at first increases with increasing concentration of sodium hydroxide. Whenever the investigation has been continued up to very high concentrations of sodium hydroxide, however, a new solid phase, referred to in every case

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[5] The most recent and apparently the most reliable of these studies are the following: (a) Goudriaan, *Rec. trav. chim.*, **39**, 505 (1920); (b) Müller, *Z. Elektrochem.*, **33**, 135 (1927); (c) Dietrich and Johnston, THIS JOURNAL, **49**, 1419 (1927); (d) Fricke, *Z. anorg. allgem. Chem.*, **172**, 234 (1928).

[6] Due, according to Dietrich and Johnston (Ref. 5 c, p. 1423), to the fact that in most cases the exact nature of the solid phase is open to question.

as sodium zincate, has been found to appear,[7] and from this point on the concentration of zinc hydroxide in the saturated solution decreases with further addition of sodium hydroxide. Obviously, from the data obtained in the present investigation, the relationships in the corresponding ternary system in acetic acid are quite analogous to those just discussed, with the ternary addition compound which occurs in the acetic acid system playing the same part as the sodium zincate in the aqueous system.[8]

This analogy now naturally brings up the question of the composition of the solid phase referred to as sodium zincate. Here again there is no agreement between the results of different investigators. Selecting those which appear to be the most reliable, we find the following formulas reported for compounds of this type: (1) $NaHZnO_2 \cdot 3H_2O$,[9] (2) $Na_2ZnO_2 \cdot 4H_2O$,[10] (3) $NaHZnO_2 \cdot 4H_2O$.[11] Still other compounds of this nature have been reported by other investigators.[12] All of these so-called sodium zincates, however, have this property in common, namely, that they may be formulated as addition compounds, generally hydrated, of the two hydroxides. Thus the formulas of the three listed above may be rewritten as follows: (1) $Zn(OH)_2 \cdot NaOH \cdot 2H_2O$, (2) $Zn(OH)_2 \cdot 2NaOH \cdot 2H_2O$, (3) $Zn(OH)_2 \cdot NaOH \cdot 3H_2O$. The similarity between such formulas and that of the solvated sodium zinc acetate isolated from the acetic acid system in this investigation is plainly evident. The resemblance between the latter compound and the hydrated disodium zincate of Goudriaan[10] is particularly close, as appears in the following comparison:

$$Zn(OH)_2 \cdot 2NaOH \cdot 2H_2O \text{ or } Na_2ZnO_2 \cdot 4H_2O$$
$$Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2 \text{ or } Na_2Zn(C_2H_3O_2)_4 \cdot 4HC_2H_3O_2$$

Discussion

It has been customary to attribute the reaction between zinc hydroxide and sodium hydroxide in aqueous solution to the so-called amphoteric nature of zinc hydroxide. This compound is thought of as possessing weakly acidic as well as weakly basic properties and as being capable, by virtue of the former, of reacting with bases to form zincates. The same point of view and system of nomenclature have been carried over

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[7] At 30°, according to Müller (Ref. 5 b, p. 140), this occurs when the concentration of sodium hydroxide reaches about 12 moles per liter. Dietrich and Johnston found only zinc hydroxide as solid phase, their investigation not having extended to concentrations of alkali sufficiently high for the appearance of sodium zincate.

[8] It should be noted that, just as the sodium zincate is unstable in the presence of water, changing to zinc hydroxide, so the ternary compound is unstable in pure acetic acid, changing to zinc acetate.

[9] Foerster and Günther, *Z. Elektrochem.*, **6**, 301 (1899).

[10] Goudriaan, Ref. 5 a, p. 508.

[11] Fricke, Ref. 5 d, p. 242.

[12] See Comey and Jackson, *Am. Chem. J.*, **11**, 145 (1899); also Müller, Ref. 5 b, p. 139.

to the ammonia system of compounds.[13] Thus, when it was found by Fitzgerald that zinc amide reacted with a liquid ammonia solution of potassium amide to give a crystalline product whose formula could be written $Zn(NH_2)_2 \cdot 2KNH_2$, or $Zn(NHK)_2 \cdot 2NH_3$,[14] this new compound was immediately named potassium ammonozincate, and its formation was cited as evidence of the amphoteric nature of zinc amide.[15] With these precedents in mind, and in view of the composition and mode of formation of the new compound, $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$, obtained in the present investigation, it would appear to be entirely logical to call this compound, provisionally at least, sodium acetozincate, and to regard its existence as supplying further confirmation of the amphoteric nature of zinc. It must be borne in mind, however, that no evidence has as yet been obtained for the presence, in acetic acid solution, of analogs of the zincate ions, ZnO_2^{--} and $HZnO_2^{-}$, which are supposed to exist in aqueous solution. Preliminary experiments have indicated that the solubility of a number of other acetates in acetic acid is also increased by the presence of sodium acetate. Further investigation of these systems will be necessary, therefore, before it can be decided whether or not the concept of amphoterism[15b] affords the most satisfactory interpretation of their behavior.

Reactions of Zinc Salts in Acetic Acid Solution.—The quantitative study of solubilities reported above was supplemented by a few further experiments of a qualitative nature, the results of which appear to the writers to be of sufficient interest to warrant brief description here.

Metallic zinc did not react noticeably with pure acetic acid at room temperature; on heating, a slight reaction occurred, with the evolution of hydrogen and the appearance of insoluble zinc acetate. With a solution of dry hydrogen chloride, zinc reacted fairly readily, giving a clear solution; after a time a precipitate appeared, doubtless consisting of zinc chloride. With a solution of sodium acetate zinc gave no noticeable reaction until the mixture was heated, when the evolution of hydrogen took place more rapidly than with pure acetic acid; in this case no insoluble product was formed. This last reaction appears to be analogous to the action upon zinc of aqueous sodium hydroxide solution.

Zinc acetate dissolved readily in the calculated amount of hydrogen chloride solution to give a clear solution of zinc chloride, which was used in the following tests. When a small amount of ammonium acetate solu-

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[13] See Franklin, *Am. Chem. J.*, **47**, 307 (1912), and THIS JOURNAL, **37**, 2295 (1915).

[14] Fitzgerald, *ibid.*, **29**, 656 (1907); see also Franklin, *ibid.*, **29**, 1274 (1907). It should be mentioned that this compound is stable in the presence of liquid ammonia, in which it is but slightly soluble.

[15] (a) Franklin, *ibid.*, **35**, 1455 (1913). See also (b) Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 175 (1924), where the concepts of amphoterism and amphoteric properties of elements are discussed at some length.

tion was added to zinc chloride, a heavy precipitate of zinc acetate was formed after a few minutes. This precipitate dissolved readily in excess ammonium acetate. Similarly, a small amount of sodium acetate solution, added to zinc chloride, produced a precipitate[16] which dissolved readily in excess sodium acetate. Thus, just as zinc hydroxide, insoluble in water, dissolves in hydrochloric acid or in aqueous sodium or ammonium hydroxide, so zinc acetate, insoluble in acetic acid, dissolves in a solution of hydrogen chloride or of sodium or ammonium acetate in this solvent.

The precipitation of zinc sulfate upon the addition of sulfuric acid solution to zinc chloride, and of zinc sulfide upon the introduction of gaseous hydrogen sulfide, have been mentioned previously.[17] The latter precipitate was found to occur even in the presence of a small concentration of hydrogen chloride, but took place more readily in the absence of the latter, that is, in what might be spoken of as a "neutral" solution.[18] The precipitate dissolved when excess of hydrogen chloride solution was added.

Solutions of sodium oxalate and of orthophosphoric acid gave with zinc chloride white precipitates of the oxalate and phosphate, respectively, both of which dissolved readily in hydrogen chloride solution.

It may be noted that all of these qualitative observations, as well as those reported previously, point toward the generalization that if a salt is insoluble in water, it will be found to be insoluble in acetic acid also; if it is readily soluble in water, however, it may or may not be soluble in acetic acid.

Summary

1. The solubility of zinc acetate in pure acetic acid and in the presence of concentrations of sodium acetate up to about 7 mole per cent. has been determined at various temperatures.

2. The concentration of zinc acetate in the saturated solutions has been found to increase with increasing concentration of sodium acetate as long as zinc acetate itself is the stable solid phase, but to decrease with further addition of sodium acetate after the appearance of an addition compound as solid phase.

3. A solvated sodium zinc acetate of the formula $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$ has been isolated and analyzed.

4. Attention has been called to the marked analogy between the ternary system here studied and the corresponding aqueous system.

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[16] In this case the precipitate was obtained more readily from a zinc chloride solution prepared by heating hydrogen chloride solution with excess zinc acetate and filtering.

[17] Ref. 3, p. 1893.

[18] In this connection, it is worthy of note that cobalt and nickel sulfides could be precipitated from dilute solutions of their chlorides only in "basic" solution, that is, in the presence of sodium acetate, for example.

5. Some further reactions of zinc salts in acetic acid solution have been described.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

PHOTOCHEMICAL STUDIES. X. THE ELECTRONIC AND PHOTOCHEMICAL DECOMPOSITIONS OF POTASSIUM CHLORATE

BY JOHN G. MEILER AND W. ALBERT NOYES, JR.

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The chemical effects of alpha and beta particles have been studied in some detail during the past few years.[1] These studies have served to demonstrate an equivalence between the extent of ionization and the amount of chemical reaction produced. It has also been shown[2] that reactions initiated by electron bombardment obey laws very similar to those applicable to α-particles. Other reactions have been studied in an effort to determine the minimum kinetic energy of electron which will produce an effect. Thus ammonia is formed in a mixture of nitrogen and hydrogen when these gases are under the influence of electrons of speed greater than those corresponding to the ionization potentials of both reacting gases.[3]

The present work was undertaken with the object of ascertaining whether solid potassium chlorate could be decomposed by slow speed electrons and to ascertain whether any relationship could be found between the kinetic energy of the electrons and the wave length of radiation necessary to bring about photochemical decomposition. The conditions for photochemical decomposition have been obtained, but the results on the electronic decomposition are somewhat less conclusive. They indicate, however, that solid potassium chlorate may be decomposed by fairly high speed electrons.

I. Experimental Procedure

(a) **The Electronic Decomposition.**—Preliminary studies[4] indicated that solid oxalic acid could be decomposed by electron bombardment

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[1] For review, see Lind, "The Chemical Effects of Alpha Particles and Electrons," 2d ed., The Chemical Catalog Co., Inc., New York, **1928**.

[2] See, for example, Marshall, THIS JOURNAL, **50**, 3178 (1928); Busse and Daniels *ibid.*, **50**, 3271 (1928); Kruger and Moeller, *Physik. Z.*, **13**, 1040 (1912); Kruger and Utesch, *Ann. Physik*, **78**, 113 (1925).

[3] Hiedeman, *Chem.-Ztg.*, **45**, 1073 (1921); **46**, 97 (1922); Anderson, *Z. Physik*, **10**, 54 (1922); Storch and Olson, THIS JOURNAL, **45**, 1605 (1923).

[4] For mention, see Noyes and Vaughan, *Chem. Reviews*, (to appear in the near future).