tion 1, but that reaction 2 takes place with difficulty and is aided materially by the excess quantum energy carried off by HCO in the primary process. As the energy in excess of that necessary to break the C–C bond became greater the efficiency of reaction 2 would be increased. The HCO not reacting in this way would go to form some of the condensable molecules mentioned above. Sufficient information is not available at the present time to permit a choice between these alternatives pertaining to the primary process. However, in view of the interest which has been manifest concerning this point, it may be well to point out that although the production of some carbon monoxide and hydrocarbon in the initial act of absorption is not excluded from the possibilities, there appears to be little evidence which requires this reaction.

It should be mentioned that λ 2000–2100 occurs in a second general region of absorption and that the failure to obtain volatile decomposition products in this region is in agreement with the early work of Henri and co-workers.[14]

Summary

1. A study of the volatile decomposition products obtained in the photolysis of acetaldehyde has been made. The products are methane, hydrogen and carbon monoxide *only*.

2. A detailed study of the hydrogen to carbon monoxide ratio has been made in a series of experiments in which pressure, intensity of radiation, temperature and wave length were in turn made the variable. This ratio was found to decrease with increase in pressure; to increase with increase in intensity; to increase with decrease in wave length; and to go through a maximum at about 30° when temperature was varied.

3. A tentative chain mechanism of photolysis similar to that given by Leermakers for elevated temperature decomposition has been proposed.

4. The experimental results indicate that there is a close correlation between the volatile and the so-called polymerization products and that in order to arrive at the correct interpretations of aldehyde photodecomposition more must be known about the resinous material which is formed.

LOS ANGELES, CALIF. RECEIVED MARCH 9, 1938

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[14] Henri and Wurmser, *Compt. rend.*, **156**, 230 (1913); Henri and Bielecki, *ibid.*, **155**, 456 (1912).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Inorganic Phosphors without Metallic Activator

BY WILLIAM H. BYLER

Introduction

The fluorescence of teeth suggests the existence of a type of fluorescent substance differing from the more familiar phosphor resulting from firing a salt with a small amount of foreign metal as activator. Following this suggestion, Glasser and Fonda[1] found that a co-precipitated mixture of calcium phosphate and tartrate developed fluorescence similar to that of teeth upon firing at 400°. This result appears to be particularly significant because it indicates that a foreign anion may serve as activator. Continuing this work, it was found by the writer that a phosphor with luminous intensity about equal to that of the phosphate–tartrate mixture could be made by treating calcium phosphate with phosphoric acid and firing at 400°. An attempt is made in this paper to correlate these types of fluorescent calcium phosphate and to show their relation to phosphors prepared by heat treatment of other salts and salt complexes.

Phosphors from Heat Treatment of Simple Compounds.—Light is thrown on the mechanism of phosphor formation in mixtures of salts by study of phosphors formed from simple compounds. A few compounds which could be expected to produce on heat treatment a complex made up of different compounds or different crystal forms were selected. Most of the products showed fluorescence in the visible region in response to the 3650 Å. line of mercury radiation. The hydrates of zinc sulfate, magnesium sulfate, and strontium chloride developed fluorescence when heated at temperatures which effect partial dehydration. In this type of preparation the fluorescence is reduced by overheating. Barium chloride was made fluorescent by heating it above its transition temperature. The hydroxides of aluminum, calcium, and mag-

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[1] J. Glasser and G. R. Fonda, THIS JOURNAL, **60**, 722 (1938).

nesium developed fluorescence as a result of partial decomposition. A fluorescent combination of magnesium hydroxide and oxide was also obtained by soaking crystals of the oxide in warm water overnight. Three of the calcium phosphates, hydroxyapatite, tricalcium phosphate, and dibasic phosphate, developed fluorescence when fired separately at 400°. Purity of the tricalcium phosphate was, however, questionable.

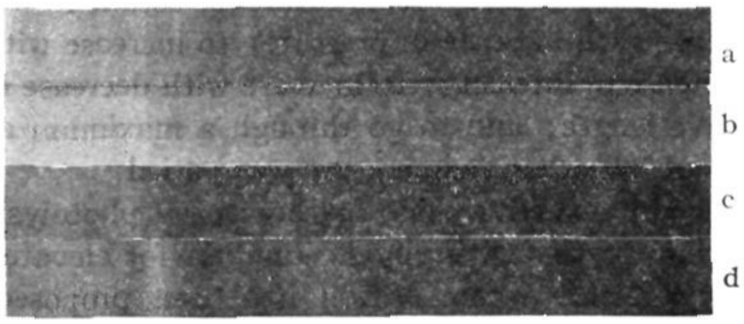

Fig. 1.—X-Ray powder patterns: a, $CaHPO_4$ before firing; b, $CaHPO_4$ fired at 400°; c, $CaHPO_4$ fired at 800°; d, acid aged hydroxyapatite fired at 400° (same pattern before treatment).

The case of dibasic calcium phosphate was studied in more detail. The salt was precipitated from calcium chloride with a sodium phosphate solution of *p*H 5.5, and was allowed to stand in the acid solution overnight before washing and drying. Samples of the ground material were fired at different temperatures for a period of one hour. The resulting fluorescence intensities and weight losses are given in Table I. In testing the fluorescence, the source used was a capillary mercury arc lamp with Corning filter No. 586, limiting the radiation to the region 3300–3900 Å. with a peak at 3650 Å. Measurements of fluorescence intensity were made with a MacBeth illuminometer. The values refer to scale readings where 14.5 corresponds to a brightness about 5% of that of grade A fluorescent zinc sulfide.

TABLE I

VARIATION OF FLUORESCENCE AND WEIGHT LOSS OF $CaHPO_4$ WITH FIRING TEMPERATURE

Temp., °C.	Wt. loss, %	Fluorescence	Fluorescent color
Dried	..	Trace	....
350	12.2	2.57	Blue
400	13.7	2.78	Yellow
450	15.4	1.46	Orange-yellow
800	16.5	0	....

Complete decomposition of anhydrous dibasic phosphate to form pyrophosphate corresponds to a loss of weight of 6.4%. Since dehydration is complete at 350°, it is necessary to conclude that optimum fluorescence corresponds to a partial decomposition of the dibasic phosphate. The similar case of partial decomposition of zinc carbonate resulting in a phosphor was studied by Beutel and Kutzetnigg.[2] The product yielding maximum fluorescence was found to contain 0.11 mole per cent. of zinc oxide.

The changes effected in the phosphate by heat treatment were revealed by X-ray powder patterns, as shown in Fig. 1. The 400° pattern appears to represent a mixture of the original phosphate with a new substance, while 800° treatment results in a complete change to a new substance, presumably pyrophosphate. The luminescence of this type of phosphor evidently depends upon a partial change to a new crystal species, probably resulting in a distortion of the lattice.

Mixed Calcium Phosphates.—When a precipitated mixture of different calcium phosphates was washed and fired at 400°, a phosphor with luminous intensity higher than that produced from any of the pure phosphates was obtained. Foreign salts are readily adsorbed on such precipitates, but no foreign inorganic anion was found to serve as activator, while some of them proved to be quite poisonous. The active complex involves only substances resulting from heat treatment of the phosphates of calcium. Experiments will be described which show (1) that other prefiring variables are secondary in importance to composition; (2) that dibasic phosphate, $CaHPO_4$, and hydroxyapatite, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$, make up the most favorable pre-firing mixture; (3) that the proportion of these compounds is critical; and (4) that formation of the fluorescent complex by heat treatment depends upon modification of the phosphate mixture accompanied by a distortion of the apatite lattice. This modification is probably due largely to decomposition.

The Acid Effect.—In developing a standard procedure for use in a study of the acid effect, a number of variables with significant bearing on the quality of the product were discovered. Keeping the compositions and concentrations of the precipitating solutions constant, the significant variables are as follows: (1) temperature of solutions, (2) rate of precipitation, (3) extent of aging of precipitate, (4) extent of washing, (5) drying temperature and period, (6) humidity of

(2) E. Beutel and A. Kutzetnigg, *Monatsh.*, **70**, 297–301 (1937).

atmosphere around material between drying and firing, (7) temperature and period of firing. Some of these seem to indicate that the physical condition of the mixture both before and after firing is important.

Precipitation from calcium chloride and normal sodium phosphate produced a mixture of calcium phosphates which was washed by centrifuging and decanting. Other variables were held constant. The powders were fired for one hour at 400°. The results of some of these experiments are given in Fig. 2, where fluorescence in scale readings is plotted against number of 40-cc. washes for different concentrations of acid.

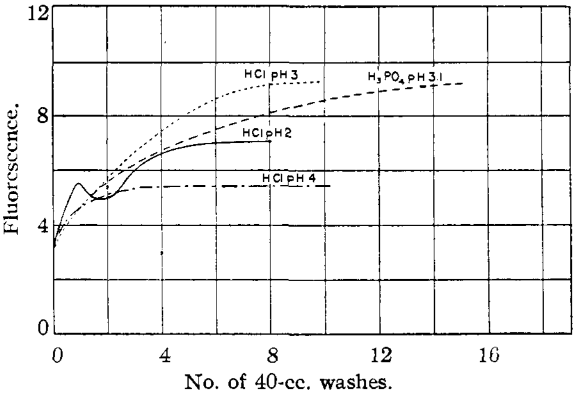

Fig. 2.—Effect of acid washing on fluorescence of calcium phosphate.

The curves of Fig. 3 represent the *p*H values of the wash solutions measured with the Beckmann glass electrode *p*H meter. Curves of similar shape result from washing with water. The low *p*H of the mother liquor shows that the precipitate contains some basic phosphate. It is known that tricalcium phosphate slowly undergoes hydrolysis to form hydroxyapatite and phosphoric acid. The curves indicate that solution of some of the hydroxyapatite has a marked effect on the *p*H of the first few wash solutions. The *p*H 3.1 curves show the effect of aging the precipitate overnight.

Coincident with the initial increase in acidity of the solid there is a rise in the fluorescence after firing at 400°. But there is evidently an optimum acid concentration and a corresponding optimum ratio of the phosphates. The fluorescence is very sensitive to small changes in composition near the optimum. X-Ray patterns of a number of these samples all showed the apatite structure the same as that of the mineral apatite, and revealed no effects from washing with acid nor from firing at 400°.

The optimum mixture was also obtained by precipitation from sodium phosphate solutions of varying *p*H. Glass and Jones[3] state that almost any proportion of the di- and tribasic phosphates is obtainable in this way. This approach also allows determination of the aging effect independent of composition. Since the same peak fluorescence was reached, the composition is the most significant pre-firing variable, and all of the variables mentioned at the beginning of this section can be explained in terms of this one, with the possible exception of period of drying. The slight increase resulting from extended treatment at 110° may be due to diffusion.

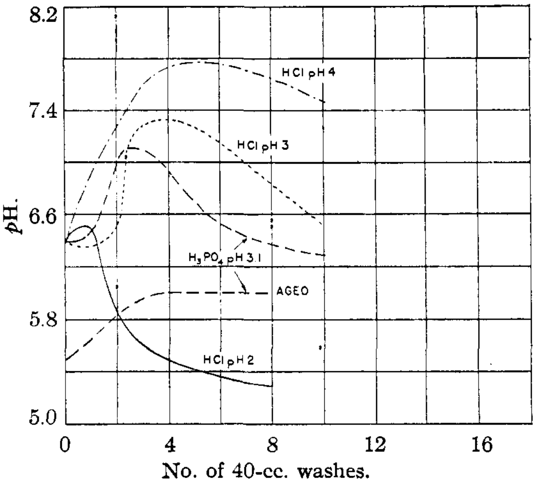

Fig. 3.—*p*H of wash solutions against number of washes for calcium phosphate.

Acid-Aging of Hydroxyapatite.—Another approach to the problem of the nature of the active complex was made by using the basic phosphate, hydroxyapatite, as starting material, and slowly transforming it to the acid phosphate by aging in phosphoric acid. Following the suggestion of Trömel and Möller,[4] hydroxyapatite was precipitated from ammoniacal calcium chloride by adding normal sodium phosphate slowly with constant stirring. An attempt also was made to prepare pure tricalcium phosphate by the method of Withers and Feild.[5] Samples of these preparations and of those resulting from various periods of acid-aging were fired at 400° with the results shown in Fig. 4. The peak fluorescence is about the same as that found by the other methods,

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[3] N. Glass and A. J. Jones, *Quart. J. Pharm. Pharmacol.*, **5**, 442–453 (1932).

[4] C. Trömel and H. Möller, *Z. anorg. allgem. Chem.*, **206**, 227–240 (1932).

[5] W. A. Withers and A. L. Feild, THIS JOURNAL, **37**, 1091 (1915).

and the curves show the rise and fall in fluorescence which accompanies a gradual change from hydroxyapatite through mixtures of the phosphates to pure dibasic phosphate. Acid of *p*H 2.3 takes the mixture through the optimum composition and far into an acid phosphate excess when stirred with the precipitate. The *p*H 1.9 acid is too strong to allow approach to the optimum, but brings the final product almost to pure dibasic phosphate.

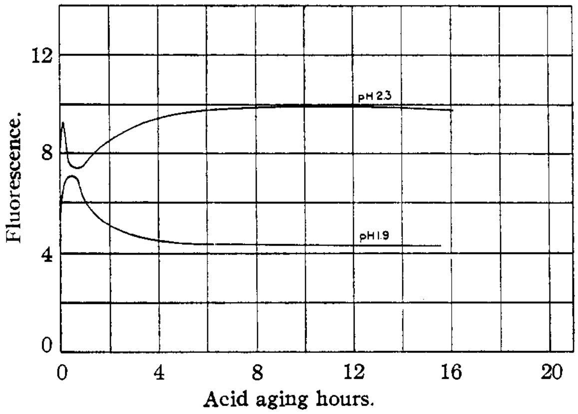

Fig. 4.—Effect of acid aging of calcium phosphate on fluorescence.

The X-ray patterns for samples represented by the curves, one of which is shown in Fig. 1, reveal only the apatite structure and show a marked decrease in particle size as the aging progresses. However, a sample aged for one week in the strong acid shows the dibasic phosphate structure. Since the initial and end products, hydroxyapatite and dibasic phosphate, respectively, exhibit only a low order of fluorescence, and since the nearly pure tricalcium phosphate exhibits a similarly low fluorescence, we may conclude that the optimum fluorescence, amounting to about four times that of the pure materials alone, is characteristic of an intermediate product, having a particularly favorable proportion of hydroxyapatite and dibasic phosphate. The content of dibasic phosphate is, however, too low to register on an X-ray pattern.

Mixing of Acid Phosphate and Hydroxyapatite.—Further proof that it is a particular mixture of dibasic phosphate with a more basic phosphate which gives rise to optimum fluorescence was obtained by mixing directly the pure compounds and firing at 400°. The results are given in Table II. The weighted average is figured on the basis of the pure materials fired at 400°. It is clear that a simple mechanical mixture is not effective and that efficiency of activation depends upon the extent to which intimacy of mixture can be produced.

TABLE II

FLUORESCENCE OF MIXTURES OF ACID AND BASIC PHOSPHATES

Method of mixing	% of $CaHPO_4$	% fluorescence above weighted average
	5	18
Ground together	10	21
dry	20	37
	50	30
Ground together wet	50	68
Ground separately and mixed	50	− 9
with glass rod	75	−14

Mechanism of Phosphor Formation.—The proportion of dibasic phosphate in the optimum mixture resulting from acid-aging is evidently too low to cause on firing a distortion of the apatite lattice which can be detected in the X-ray pattern. However, a slight contraction of the lattice was indicated in the pattern from a sample which was aged in weak acid for one week. Such a complexity in the crystal structure was observed also in the phosphor obtained from dibasic phosphate alone. In both cases, then, the function of the firing is evidently to form a critical crystalline complex. The optimum final condition in the case of the mixed phosphates corresponds to a critical proportion of the phosphates before firing as well as to proper heat treatment. The product, so to speak, is a double complex—a complex formed by critical thermal modification of a critical complex.

Further information on the changes accompanying phosphor formation was obtained by studying the growth of fluorescence as a function of firing period at different temperatures. The growth rate was found to correspond neither to a first order nor to a second order change. If the rate-controlling process were the decomposition of dibasic phosphate to form pyrophosphate and water, the second order law should apply. But progress of this reaction depends upon diffusion of the dibasic phosphate, and since it is uniformly distributed in the beginning, the rate of diffusion should correspond to a first order change. It is, therefore, suggested that the rate of diffusion of water out of the grains is an important factor. Since there is probably not a uniform concentration gradient for water, the rate is not expected to fit the first order law.

Other Inorganic Mixtures

The case of the calcium phosphates led to trials on other mixtures of similar nature and on other mixtures of two compounds which could be expected to be closely associated, one of which could be transformed or decomposed by heat treatment to give a new structure.

Strontium phosphate and zinc phosphate both developed a low order fluorescence when treated by methods used for calcium phosphate. Magnesium phosphate approached calcium phosphate in efficiency. By contrast, acid-aging of the precipitate reduced the fluorescence, whereas a co-precipitated mixture of phosphate and hydroxide gave a better product than either pure phosphate or hydroxide separately. Since pure magnesium hydroxide probably develops fluorescence through partial decomposition, it appears that we have here a case similar to that of the mixed calcium phosphates with the hydroxide serving as activator. Aluminum phosphate was found to behave in a manner similar to magnesium phosphate in every respect. A mixture of ten parts barium sulfate to one part potassium sulfate ground together and fired for one hour at 600° showed a definite response to the 2536 Å. radiation.

These results give further support to the idea that the fluorescence arises from formation of a complex, where composition and physical condition are critical.

Calcium Phosphate Activated by Organic Anions.—The results of Glasser and Fonda[1] on the phosphate–tartrate mixtures may be interpreted in the light of the behavior of the strictly inorganic mixtures. Further work was done on these phosphors with the idea of establishing the nature of the most effective mixture.

Effective mixtures of calcium phosphate and tartrate may be obtained either by co-precipitation, or by simply washing the freshly precipitated phosphate with a tartrate solution before drying and firing at 400°. Some of the variables listed for pure calcium phosphates are effective in the opposite direction for this mixture. Long aging of the precipitates, high temperature precipitation, and aging in ammoniacal solution all serve to improve the product. These are variables which tend to encourage formation of the crystalline hydroxyapatite. The tartrate was also found to activate pure hydroxyapatite prepared by the method previously mentioned. A number of other organic anions which are unstable at 400° serve as activators. It appears unlikely, therefore, that a particular decomposition product is required. It is probable that the case is quite similar to that of the mixed calcium phosphates with the unstable organic compound replacing the unstable dibasic phosphate.

This type of phosphor, involving a complex formed from calcium phosphate and an organic anion, may be prepared in another way. Calcium tartrate is decomposed by firing in air at 400° to form a mass which is largely soluble in hydrochloric acid. By nearly neutralizing the acid solution with sodium hydroxide and washing freshly precipitated calcium phosphate with it, a blue fluorescence similar to that of teeth and to that of the fired phosphate–tartrate mixture is produced without any further heat treatment. Filter paper, calcium carbonate, and calcium hydroxide also serve as bases for formation of phosphors when washed with this solution. This general phenomenon may be related to the cases discussed by Haitinger[6] in connection with fluorescence analysis, and ascribed by him to the adsorption of organic compounds. In the light of the present work, it seems preferable to regard such cases as dependent upon the formation of a complex. This is in agreement with the conclusion of Schmidt[7] drawn from his experiments with mixtures of organic dyes and various foreign materials. Since teeth are made up largely of calcium phosphate in the apatite structure and contain about 1% of organic matter, it would seem that their fluorescence may be due to the presence of this type of complex.

This work was originally suggested by Dr. W. R. Whitney. The author is glad to acknowledge his indebtedness also to Dr. G. R. Fonda for many helpful suggestions. The X-ray patterns were obtained through the courtesy of Mr. E. T. Asp and Mr. L. L. Wyman.

Summary

Phosphors have been made from a number of inorganic compounds and mixtures without use of metallic activators. The case of the calcium phosphates has been considered in detail. Whereas the pure basic phosphate and acid phosphate show fluorescent intensities of 2 and 3 on an arbitrary scale after optimum heat treatment at 400°, a proper mixture of the two develops an

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(6) M. Haitinger, "Die Fluorescensanalyse in der Mikrochemie," Verlag Emil Haim, Leipzig, 1937, p. 24.

(7) G. C. Schmidt, *Ann. Physik.* **65**, 247 (1921).

intensity of 10 when similarly treated. Phosphors developed from mixtures of calcium phosphate with certain organic compounds have been studied in the light of results from the purely inorganic cases.

These experiments have led to the general conclusion that, in the absence of a specific metallic activator, fluorescence resulting from heat treatment of inorganic compounds is due to formation of complexes of critical composition through partial decomposition or of critical physical condition through modification of crystal structure.

SCHENECTADY, NEW YORK RECEIVED MARCH 11, 1938

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE AND COLUMBIA UNIVERSITY]

Acid Dissociation Constants in Dioxane–Water Mixtures by Potentiometric Titration

BY CECIL C. LYNCH AND VICTOR K. LA MER

While potentiometric acid–base titrations in aqueous solutions have been examined exhaustively both with respect to theory and practice by many workers,[1–9] comparatively few investigations have been made in non-aqueous and mixed solvents. In this connection the work of Bishop, Kittredge and Hildebrand[10] in ethyl alcohol, of Clark, Wooten and Compton,[11] and Wooten and Hammett,[12] in *n*-butyl alcohol should be mentioned. Likewise, La Mer and Downes[13] have shown the possibility of acid–base titration in benzene, and Tomicek[14] has made titrations of weak acids in several mixed solvents. Since dioxane–water mixtures offer a continuous transition from a polar aqueous to non-polar solvent, a study of the titration of weak acids in such mixtures presented a significant problem.

The unusual and complicated conductivity titration curves obtained by La Mer and Downes[13] for electrolytes in benzene and the equally complicated conductivity dilution curves obtained by Fuoss and Kraus[15] for salts in dioxane–water mixtures stimulated us to investigate whether or not the e. m. f. titration curves would be simple or complex in low dielectric solvents.

Dioxane–water mixtures were selected for several reasons. This cyclic ether mixes with water in all proportions, giving a wide range of dielectric constant; it is becoming more and more important as a solvent for many substances which are practically insoluble in water: for example, the commercially important resin acids, like abietic acid. Also, many related physical properties[16,17] of the aqueous mixtures are rapidly becoming available in the literature.

In preliminary work on potentiometric titrations of weak acids in dioxane–water mixtures, the titration curves did not yield results in agreement with the Nernst relation. This finding encouraged further investigation and led to the results here presented.

Theory of Acid–Base Titrations.—Auerbach and Smolczyk[1] employed the relation

$$K = m_{\mathrm{H}}(X/1 - X) \qquad (1)$$

for monobasic acids for the acid region, where K is the dissociation constant (classical); m_{H} is the concentration of the hydrogen ion; X is the fraction of the acid neutralized. They assumed that all salts were completely dissociated and that the concentrations were so low that the activity coefficients for univalent ions could be taken as unity. Söderbäck[2] in an elaborate and thorough treatment modified this relation by introducing the activity coefficient and the thermodynamic dissociation constants. His relation is

$$K^0 = fm_{\mathrm{H}}\,(B/(B - 1)) \qquad (2)$$

where $B = (mx/cv_0) + (m_{\mathrm{H}}/c)\,(1 + x/v_0)$; m is molarity of the base; x is volume of base used; c is initial concentration; v_0 is initial volume of acid solution; f is activity coefficient of univalent ions. Eq. (2) is not significantly different from

$$K^0 = fm_{\mathrm{H}}(X/(1 - X)) \qquad (3)$$

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(1) Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

(2) Söderbäck, *Arkiv. Kemi. Min. och. Geol.*, **11A**, 1 (1934).

(3) Brönsted, *Z. physik. Chem.*, **169**, 52 and 361 (1934).

(4) Larsson, *ibid.*, **156**, 352 and 381 (1931); **157**, 342 (1931); **159**, 306 and 315 (1932); **165**, 53 (1933).

(5) Hahn, *Ber.*, **62B**, 727 (1929); *Z. angew. Chem.*, **43**, 712 (1930); *Z. physik. Chem.*, **127**, 1 (1927).

(6) Gane and Ingold, *J. Chem. Soc.*, 1594 (1928); 2158 (1931).

(7) Ashton and Partington, *Trans. Faraday Soc.*, **30**, 598 (1934).

(8) Roller, THIS JOURNAL, **54**, 3485 (1932); **50**, 1 (1928).

(9) Eastman, *ibid.*, **47**, 332 (1925).

(10) Bishop, Kittredge and Hildebrand, *ibid.*, **44**, 135 (1922).

(11) Clark, Wooten and Compton, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 321 (1931).

(12) Wooten and Hammett, THIS JOURNAL, **57**, 2289 (1935).

(13) La Mer and Downes, *ibid.*, **53**, 888 (1931).

(14) Tomicek, *Coll. Czech. Chem. Com.*, **6**, 408 (1934).

(15) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

(16) Åkerlöf and Short, *ibid.*, **58**, 1241 (1936).

(17) Hovorka, Schaefer and Dreisbach, *ibid.*, **58**, 2263 (1936),