[CONTRIBUTION FROM THE PHYSICAL LABORATORY, UNIVERSITY OF DENVER, AND THE JONES CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THERMOLUMINESCENCE IN GLASSES WHICH CONTAIN TWO ACTIVATORS

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RECEIVED SEPTEMBER 15, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

It is generally accepted that the property of luminescence may be conferred upon a solid substance by the addition of certain materials which are termed activators. The variation of luminescence with the concentration of a single activator has been studied by many workers.[1] Mathematical developments of the relation between the intensity of fluorescence and the concentration of an activator in solid solutions have been made by Brüninghaus[2] and Merritt.[3] The luminescence produced by two activators in a solid material, each acting in the presence of the other, is the subject with which this paper is concerned.

Method of Making Samples and Determination of Thermoluminescence.—The material chosen as the solid solvent was a zinc borate glass. In previous experiments[4] it had been found that a similar material could be reproduced exactly, and that activators could be uniformly dispersed within this medium. Manganese and cerium were selected as the activators because the glasses which contain them are only slightly colored, within the range of concentrations to be studied. The individual glasses were prepared as follows. To 16.5 g. of glass mixture were added the computed quantities of C. P. manganous carbonate and cerous oxalate. The glass mixture contained C. P. boric acid and zinc oxide in the ratio of six parts by weight of the former to five of the latter. These had been thoroughly mixed in a quartz pebble tube mill. The mixture for the given sample, containing the manganese and cerium salts, was placed in a covered platinum crucible and heated in a gas muffle until the molten material was entirely clear and free from bubbles. The glass was then poured into a graphite mold previously heated to 400°. The glass cast and its mold were immediately placed within an electric furnace at 400° after which the glass was allowed to cool to room temperature within the furnace. The glass was then ground and polished on the two faces until the thickness was ap-

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[1] Kowalsky and Garnier, *Compt. rend.*, **145**, 391 (1907); Urbain, *ibid.*, **147**, 1472 (1908); Brüninghaus, *ibid.*, **149**, 1375 (1909); F. Perrin, *ibid.*, **178**, 1978 (1924); Engle and Hopkins, *J. Optical Soc. Am.* **11**, 599 (1925); Wawilow, *Z. Physik*, **31**, 750 (1925); Nichols and Slattery, *J. Optical Soc. Am.*, **12**, 449 (1926); Nyswander and Cohn, *ibid.*, **20**, 131 (1930).

[2] Brüninghaus, *Compt. rend.*, **149**, 1375 (1909).

[3] Merritt, *J. Optical Soc. Am.*, **12**, 613 (1926).

[4] Nyswander and Cohn, *ibid.*, **20**, 131 (1930).

proximately 2.7 mm. and the small plate was cut into squares 6 mm. on a side.

The thermoluminescence of the glasses was next determined. Before each determination the samples were heated to 300° and allowed to cool to room temperature within an electric furnace to drive off any luminescence. The samples were exposed to a quartz mercury arc to excite the thermoluminescence. The glasses were exposed for ten minutes at a distance of 20 cm. from a "Lab-Arc," the latter being operated on alternating current at sixty cycle frequency and with a current of 1.50 amperes. The glasses were removed to a dark room and allowed to remain for eight hours before measurement. This precaution was taken to remove the error due to the decay of luminescence within the glass, which is quite rapid immediately after excitation. The intensity of thermoluminescence at 100° was measured by a polarization photometer with a radioactive source as the standard of intensity of the type described by Nyswander and Lind.[5] The method of measurement is described by Nyswander and Cohn.[6]

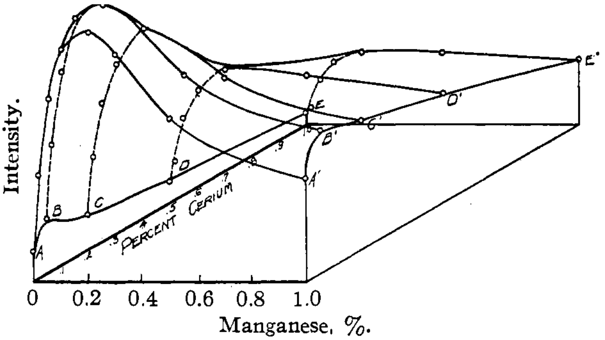

Fig. 1.—Diagram of the surface which represents the intensities of thermoluminescence of zinc borate glasses which contain both manganese and cerium, when a mercury arc is the source of excitation.

Results of Luminescence Measurements.—The intensities of thermoluminescence of a large number of samples which contain both manganese and cerium were obtained. As the intensity of the luminescence depends both upon the concentration of the cerium and that of the manganese, the intensities of luminescence when graphed form a surface. The form of surface in this case is suggested by Fig. 1. In this projection diagram the observed intensities are plotted as ordinates above the plane of concentrations. Curve A to A′ represents the intensity of thermoluminescence in samples which contain 0% of cerium and varying quantities of manganese from 0 to 1%. In a like manner Curve B to B′ gives the intensity in samples which

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[5] Nyswander and Lind, *J. Optical Soc. Am.*, **13**, 651 (1926).

[6] Nyswander and Cohn, *ibid.*, **20**, 131 (1930).

contain 0.05% cerium and varying amounts of manganese and similarly for the remaining curves. A better representation of the actual shape of the surface which gives the luminescence is obtained from the photograph of a model, as shown in Fig. 2. In this photograph the interval between two adjacent black lines represents 0.2% change in the concentration. The zero coördinate is at the corner of the base hidden from view. It will be noted that the glass itself, though made from C. P. materials, is slightly thermoluminescent.

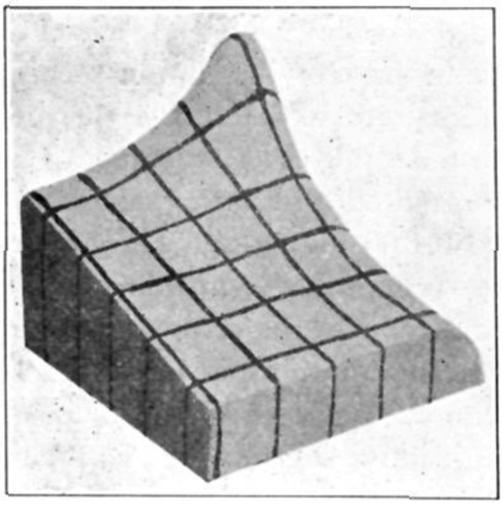

Fig. 2.—Photograph of a model of the surface indicated by Fig. 1.

Figure 3 shows the change in the intensity of the thermoluminescence of the glasses with the concentration of cerium when the concentration of the manganese is held constant. The curves represent the amounts of manganese as follows: A, 0; B, 0.02; C, 0.05; D, 0.1; E, 0.2; F, 0.5, and G, 1.0% cerium.

Figure 4 is similar to Fig. 3 except that in this set of curves the concentrations of cerium are constant for each curve. Curve A represents the change of the intensity of thermoluminescence with the concentration of manganese when 0% of cerium is present. The amounts of manganese are: Curve B, 0.05; C, 0.1; D, 0.2; E, 0.5, and F, 1.0%.

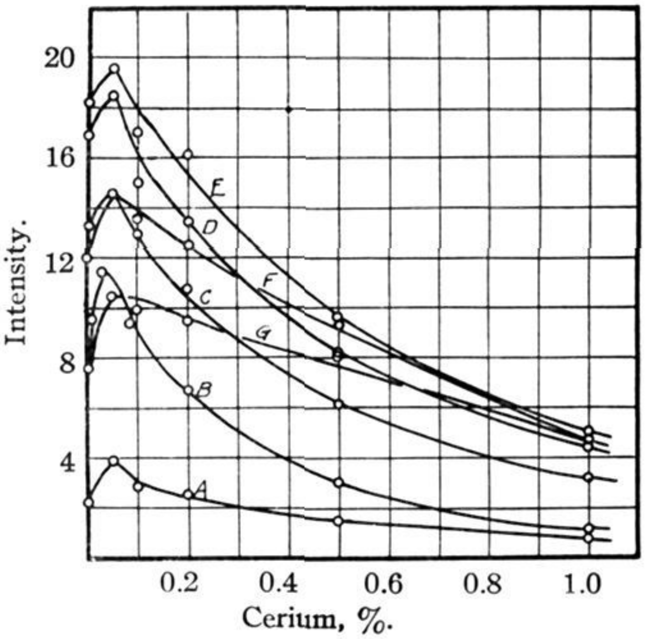

Fig. 3.—The intensity of thermoluminescence of zinc borate glasses which contain both cerium and manganese. The concentration of manganese is constant for each curve.

In Fig. 5 the intensity of thermoluminescence for glasses, each of which contains 0.02% manganese, is plotted as the ordinate and the cerium concentration of the individual glasses as the abscissa. This curve is typical of the curves for glasses which contain both manganese and cerium. It has been separated from the remaining curves of Fig. 3 for the purpose of indicating the damping action of the second activator, cerium, upon the manganese. If there were no such effect the intensity of the luminescence would approach the dotted line of the figure since the percentage of manganese remains constant; instead it falls below as indicated. The damping seems to be the same phenomenon observed qualitatively in the fluorescence of solids by Nichols and Howes[7] and discussed by them under the heading of the dominance and suppression of activators.

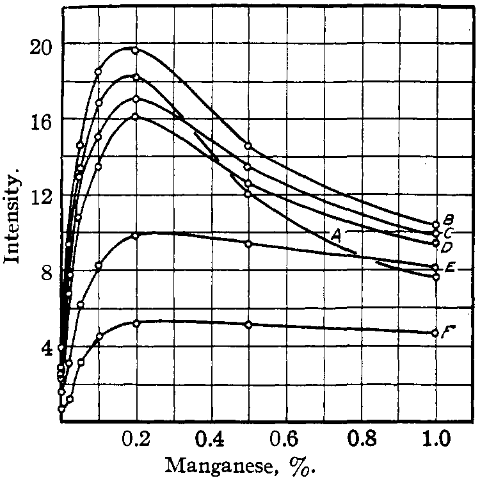

Fig. 4.—The intensity of thermoluminescence of zinc borate glasses which contain both cerium and manganese. The concentration of cerium is constant for each curve.

The effect of the cerium upon the luminescence of the manganese may be discussed from another viewpoint. A quantity, which will be termed the damping coefficient, will be defined as the ratio of the decrease in the intensity of thermoluminescence to the initial luminescence, when the decrease is caused by the addition of a fixed amount of the second activator. That is

$$\text{Damping coefficient} = \frac{I_1 - I_2}{I_1}$$

where I_1 is the intensity of thermoluminescence in a sample which contains manganese at a concentration *A*; I_2 is the intensity of thermoluminescence in a sample which contains manganese at a concentration A and cerium of concentration B. When such values are computed from the data and the damping coefficient is plotted as ordinate against the concentration of manganese (*A*) as abscissa, Fig. 6 is obtained. In this figure Curve A represents the damping coefficient for 1.0; B, 0.5; C, 0.2; D, 0.1; and E, 0.05%. When the damping coefficient is negative the cerium acts to increase the luminescence and therefore is an activator. It would appear from this figure that the same concentration of cerium may act either to damp the luminescence or to increase it. The effect of the cerium depends upon the concentration of the manganese. For ex-

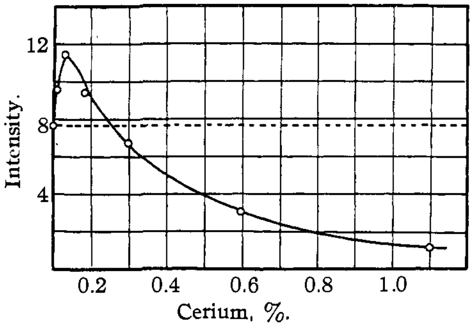

Fig. 5.—The intensity of thermoluminescence of zinc borate glasses which contain 0.02% of manganese together with cerium.

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[7] Nichols and Howes, *J. Optical Soc. Am.*, **13**, 573 (1926).

ample, from Curve C it is seen that 0.2% of cerium decreases the luminescence in all glasses which contain less than approximately 0.4% manganese, but acts as an activator in glasses which contain more than 0.4% of manganese. If the accuracy of the data permit the extrapolation, it would seem that the addition of 1% cerium, which decreases the luminescence of a 0.02% manganese glass to less than one-fifth its initial value, would slightly increase the luminescence in a sample which contains 2% manganese.

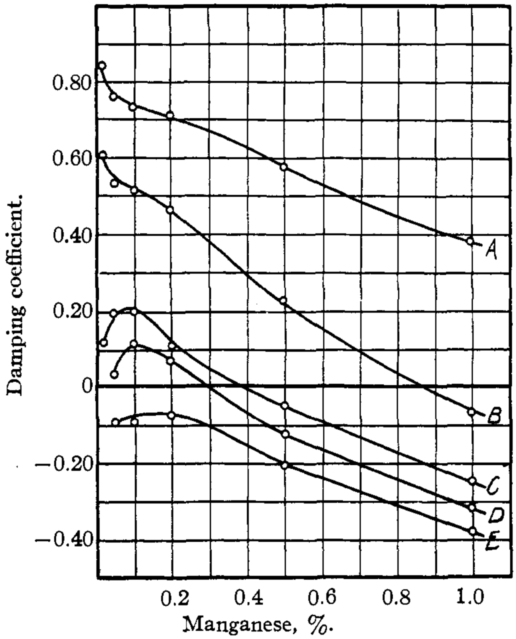

Fig. 6.—The damping coefficient as a function of the concentration of manganese in zinc borate glasses. The concentration of cerium is constant for each curve.

The Emission Spectrum of Thermoluminescence.—So far in this paper only the relative intensities of the thermoluminescent light have been discussed. Due to the low intensity of the emitted light it has not been found possible to obtain accurate spectrometric data on the thermoluminescence. However, by the use of a transmission grating, with a glowing square of zinc borate glass which contained manganese and acted as its own slit, the thermoluminescence emission was found to be a band which extends through the red, yellow and green portions of the visible spectrum. The infrared spectrum was not examined.

As the process of thermoluminescence in glasses when excited by light may be divided into the three steps: (a) the absorption of light energy, (b) the storage of the absorbed energy and (c) the emission of the stored energy, it was decided to study the absorption spectra of thermoluminescent glasses to secure more information concerning the process.

Absorption Spectra of Glasses which Exhibit Thermoluminescence.—Absorption spectra of the glasses were obtained by the use of a quartz Hilger spectrophotometer with a sector disk. The source of continuous ultraviolet light was a high frequency spark under water. The light source was constructed from the design given by Snyder.[8] From the settings on

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[8] Snyder, This Journal, 49, 2510 (1927).

the sector disk the values of the absorption coefficient K could be computed from the equation

$$\frac{I_0}{I} = e^{K\alpha d}$$

In this work I_0 is the intensity through the glass without any solute, I the transmitted intensity through glass which contains α grams of solute per 100 g. of glass and d is the thickness of the sample in centimeters. From the match point, equal density position on the spectrogram, the wave length which corresponds to K could be determined.

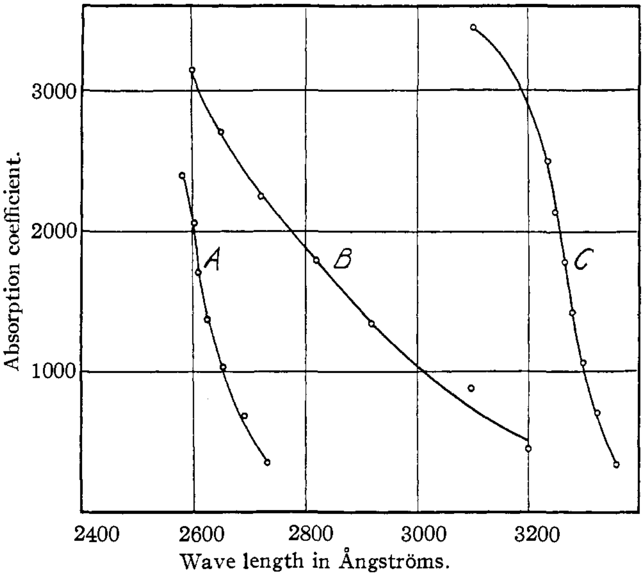

Fig. 7.—The values of the absorption coefficient K as dependent upon wave length: for zinc borate glasses which contain: Curve A, manganese; B, thorium; C, cerium.

When the values of K are plotted against the corresponding wave lengths, curves of the type shown in Fig. 7 are obtained. In this figure Curve A represents values of K obtained from a zinc borate glass which contains 0.5% manganese; B, 0.4% thorium; C, 0.5% cerium. High values of K indicate a high absorption for a given thickness and concentration. If it be assumed that these values relate to the spectral region from which the energy of thermoluminescence is absorbed, some interesting facts are indicated by the curves of Fig. 7. In the first place, absorption by these materials in glasses seems to give an absorption band only one end of which can be observed for the zinc borate glass, although a thickness of 0.27 cm. of this glass without any solute transmits well to 2500 Å., with a transmission limit close to 2400 Å. Secondly, it may be noted that for the same solvent, different light sources would show a different relative intensity of thermoluminescence for various solutes. For example, with sunlight as the source of energy, glasses which contain cerium may be expected to show a much higher intensity, relative to those which contain manganese, than when a quartz mercury arc is used as the source of excitation.

In the preceding paragraph the curves of Fig. 7 have been interpreted on the basis of the assumption that the values for K relate to the general spectral region which furnishes the energy of thermoluminescence. That this assumption has some justification is indicated by the following data. When zinc borate glass which contains 0.44% cerium was exposed to a carbon arc it was found that if the intensity of the emitted light from a square exposed directly to the source is considered to be 100, the thermoluminescent intensity from a square exposed beneath a 2.6-mm. thickness of the same glass is 3. From these values it follows that I_0/I for the exciting light which causes thermoluminescence is 33.3 and K is 3065. For this value of K in cerium glass, Curve C indicates that the mean wave length of the excitation light is 3185 Å. When the plate which gives the absorption for glass which contains 0.5% cerium is examined it is found that the absorption limit as recorded by the photographic plate varies from 3200 Å. for a ten-second exposure to 3140 Å. for a 250-second exposure. The value of 3185 Å. lies within this range and seems to give some justification to the provisional assumption that the absorption boundary for which K has been calculated is the region in which the absorbed light furnishes the energy from which the energy of thermoluminescence is derived. It is hoped that this assumption can be tested with monochromatic light, but it is difficult to obtain a sufficiently high intensity.

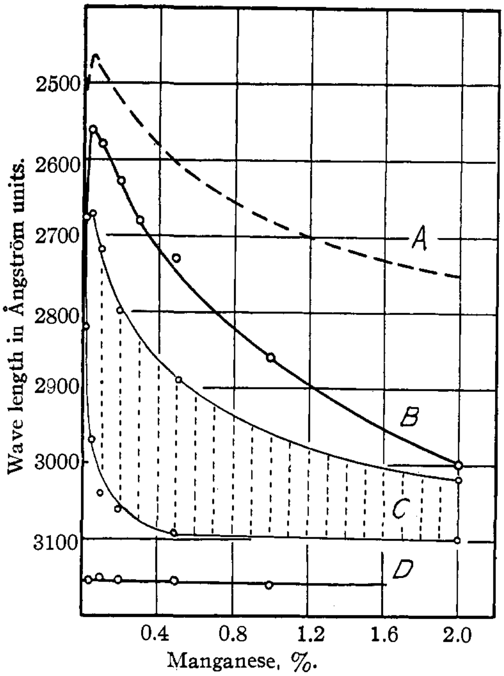

Fig. 8.—Curves B, C and D show wave lengths for which log I_0/I is equal to 0.2. Curve A represents the transmission limit for the glasses shown in curves B, C and D. Curve B represents glasses which contain zero; C, 0.02%; D, 0.05 % of cerium.

The wave lengths for which the value of log I_0/I is equal to 0.2 are shown in Curve B of Fig. 8 for zinc borate glasses which contain varying concentrations of manganese and no cerium. These are the wave lengths for which the transmission is approximately 63% of that which the glasses would have were no manganese present. If 0.02% cerium is present in addition to the manganese, the match points are definite but extend over the range indicated by the area of Curves C. With 0.05% cerium the manganese has little effect on the position of the wave lengths for which the ratio log I_0/I equals 0.2, as is exhibited by Curve D. With a sixteen-second exposure for all of the glasses, shown in Curves B, C and D, the short wave length limit of transmission obtained from the end of the spectrum on the photographic plate corresponds closely to the dotted line of Curve A. This indicates that the absorption limit of these glasses is determined by the manganese, but that the cerium determines the absorption unless the absorption is small. The form of Curve B and of Curve A, which represents the absorption limit, is unexpected. It is of particular interest since thermoluminescence is most marked in zinc borate glasses with slight concentrations of manganese and in the region affected by the anomalous absorption. Curve A of Fig. 9 gives the wave lengths for which the value of log I_0/I is equal to 0.2 for zinc borate glasses which contain varying concentrations of cerium and no manganese. If 0.02% of manganese is present in addition to the cerium, Curve B is obtained. These curves do not exhibit the anomalous behavior of the curves which represent glasses which contain manganese.

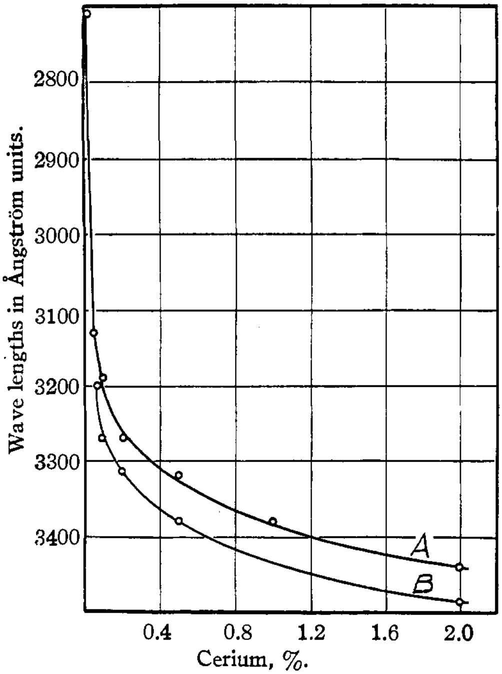

Fig. 9.—Curves which give wave lengths for which log I_0/I is equal to 0.2; Curve A represents values with zero; B, 0.02 % of manganese.

Summary

1. The thermoluminescence of glasses which contain two activators has been measured.

2. The effects of one activator upon the second are not additive. For

example, the thermoluminescence of a zinc borate glass which contains a small amount of manganese is increased by small amounts of cerium, but decreased by larger amounts. A definite amount of cerium may either increase or decrease the thermoluminescence, since the effect is dependent upon the amount of manganese present.

3. The emission spectrum for zinc borate glass which contains manganese has been found to be a band.
4. Single ended absorption bands have been found in the ultraviolet spectra with zinc borate glasses which contain manganese, cerium or thorium as the solute.
5. Intensity measurements of the thermoluminescence have been used to indicate that it is probably from near the edge of these bands that the energy for thermoluminescence is drawn.
6. From the positions of the absorption bands the conclusion is drawn that the relative thermoluminescent intensities of two materials in the same solvent changes with a change of the source of excitation.
7. Absorption curves which show the effect of cerium upon glasses which contain manganese and vice versa have been obtained.
8. An anomalous absorption has been found for zinc borate glasses which contain manganese.

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STUDIES ON HETEROPOLY ACIDS OF GERMANIUM. I. GERMANOMOLYBDIC ACID[1]

BY CHARLES G. GROSSCUP

RECEIVED SEPTEMBER 18, 1930 PUBLISHED DECEMBER 18, 1930

In the list of elements known to form heteropoly acids with molybdenum, tungsten and vanadium, one notices the absence of three members of the fourth periodic group. These elements, carbon, germanium and hafnium are missing from an otherwise complete series of the type $H_8[X(Mo_2O_7)_6]$ aq. where X may be silicon,[2] titanium,[3] zirconium,[3] thorium,[4] tin[5] and lead.[6] Possibly this may be supplemented by hafnium, which, it is conceivable, was present in the preparations of zirconomolybdates, since this element was not recognized at the time of the investigations and has since

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[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Pennsylvania.

[2] A pure acid has been obtained by Scroggie, THIS JOURNAL, **51**, 1057 (1929).

[3] Péchard, *Compt. rend.*, **117**, 781 (1893).

[4] Barbieri, *Atti. accad. Lincei*, **221**, 5, 781 (1913).

[5] Rosenheim, Pieck and Pinsker, *Z. anorg. Chem.*, **96**, 139 (1916).

[6] Ephraim, "Inorganic Chemistry," English ed., **1926**.