

closely the relative adsorption of benzoic, oxalic and hydrochloric acids by this charcoal.

The question arose whether the charcoal adsorbs from solution only the acid resulting from hydrolysis of the salt or whether part of the salt is adsorbed as such. To obtain some evidence on this question the behavior of a number of potassium salts was studied. Determination of the potassium in solution before and after adsorption indicated that from the potassium chloride solution absolutely no potassium is removed and the adsorption, therefore, is entirely hydrolytic, only hydrochloric acid being adsorbed. With potassium benzoate, however, it was found that a considerable amount of the salt as such is adsorbed in addition to the benzoic acid resulting from hydrolysis. Further evidence is being procured on this point.

Summary

1. Methods for the quantitative recovery of adsorbed acids from charcoal are described.

2. By means of these methods it has been demonstrated that when alkali is set free in salt solutions during adsorption by pure activated sugar charcoal there exists on the charcoal after adsorption an equivalent amount of adsorbed acid.

3. Data are given for the hydrolytic adsorption of a number of salts of representative organic and inorganic acids.

4. The results obtained in this investigation make untenable the present widely accepted view that hydrolytic or decomposition adsorption does not take place.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE HEAT OF WETTING OF LEAD SULFATE¹

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It has been known for the past hundred years that when some finely divided powders, or porous materials, are wetted with a liquid in which they are not soluble, the wetting is accompanied by a thermal change.²

¹ This paper constitutes a portion of a thesis presented by W. A. Koehler to the Graduate School of the University of Wisconsin, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in January, 1924.

² Pouillet, *Ann. chim. phys.*, **20**, 141 (1822). Junck, *Pogg. Ann.*, **125**, 292 (1865). Chappuis, *Wied. Ann.*, **19**, 21 (1883). Meissner, *ibid.*, **29**, 114 (1886). Fitzgerald, *Nature*, **49**, 293, 316 (1894). Gore, *Phil. Mag.*, **37**, 306 (1894). Lagergren, *Kgl. Vetenskaps Akad.*, **24B**, adf. ii (1898). Ercolini, *Nuovo cimento*, [4] **9**, 110 (1899). Linebarger, *Phys. Rev.*, **13**, 48 (1901). Parks, *Phil. Mag.*, [6] **4**, 240 (1902). Schwalbe,

The early investigations were purely of a thermometric nature, but later calorimetric investigations replaced the thermometric ones, and investigators then attempted to find the relation between surface areas and heat changes. The values obtained, however, are not concordant, for no method was known for determining definitely the surface area of any of the powders investigated.

In this investigation an attempt was made to establish the relation between the heat of wetting and the surface area when lead sulfate is wetted with water saturated with lead sulfate. By the use of radioactive isotopes of lead it is possible to determine the surface area of precipitated lead salts with a much higher degree of precision than is possible with any other powdered material.

While it was found that the heat of wetting in this particular system is zero, within the limit of experimental error, the technique is of general interest and can be applied to any system where radioactive isotopes exist.

Apparatus

The special apparatus used in this investigation consists of three parts, that for (1) drying the precipitate, (2) determining the surface area of the precipitate, and (3) making the calorimetric measurements.

The Drying of the Lead Sulfate.—It is generally known that it is extremely difficult to remove all moisture and adsorbed gases from the surface of solid materials. In this investigation the matter was further complicated by the fact that high temperatures could not be resorted to on account of the fritting or sintering of the lead sulfate particles (which would greatly reduce the surface area), and on account of the possibility of chemical decomposition of the sulfate. The method of drying used was that of a high vacuum combined with a moderate heating of the precipitate.

The drying apparatus is shown in Fig. 1.

The air-dried precipitate was placed in the bulb of the tube M which was blown to a diameter of about 3 cm. and would hold from 15 to 20 g. of the lead sulfate. The tube above the bulb was drawn to a capillary of about 1.5 mm. diameter, which served as a place for sealing off the bulb at the end of a run. The tube M was connected to the evacuating system by means of a rubber stopper which was sealed with mercury, as shown at D. A cooling coil L prevented the heating of the mercury and the stopper. The bulb of a thermometer was placed inside of the hood E.

The vacuum was obtained by the use of a Langmuir condensation pump. A mercury trap J was so placed that it protected the precipitate in the bulb from the mercury

Ann. Physik, **16**, 32 (1905). Dunlap, *J. Agr. Research*, Dept. of Agr., Project L-169, Forest Prod. Lab. (Unpublished report.) Lamb and Coolidge, *THIS JOURNAL*, **42**, 1146 (1920). Patrick and Grimm, *ibid.*, **43**, 2144 (1921). Harkins and Ewing, *ibid.*, **43**, 1787 (1921). Williams, *Trans. Faraday Soc.*, **18**, 87 (1922).

vapor from both pump and gage. The pressure of the system was determined with a McLeod gage giving accurate readings between 50 and 0.005 bars.

Two joints were placed in the system, at A and B, so that it could be taken apart into three units, for purposes of cleaning. These joints were mercury-sealed in a manner somewhat similar to the seal at D, except that the cooling coils were omitted.

It was found in the earlier runs that the pressure dropped to about 0.005 bar in eight hours or less, and that when the tube M was then tapped sharply so that the lead sulfate was jarred, the pressure immediately rose to several bars. This change in pressure upon tapping occurred even if the tapping was not begun until after the pressure had been down to 0.005 bar for five days. Within a few minutes after the tapping was stopped the pressure fell back to its former low value, but went up again after more tapping. This showed the necessity for providing a means

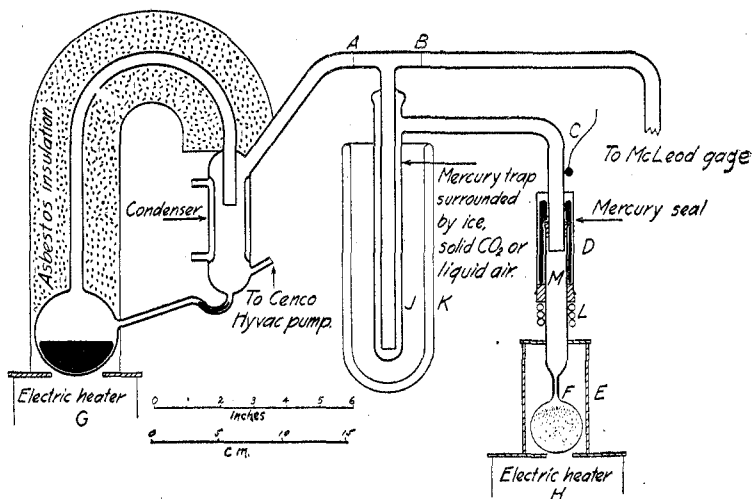


Fig. 1.

of keeping the sulfate agitated constantly so as to bring new particles to the surface, for apparently a blanket of dry and almost impervious precipitate tends to form on the surface. The agitation was accomplished without any alterations in the system except for the addition of an electric buzzer, the hammer C of which hit against the glass tube. On account of the vibration produced, the powder in the bulb gradually worked up one side of the bulb and then rolled down to the other, making a complete cycle in about half an hour. With the vibrator operating as described, a vacuum of 0.005 bar could be obtained in from 36 to 120 hours, depending upon the temperature.

At the end of a run, while the pump was still operating, the bulb containing the sulfate was sealed off. The neck of the tube was slowly softened and held at that point without sealing for about two minutes to allow

the pump to draw off gases liberated by the heated glass, and then sealed off as quickly as possible.

Determination of the Surface Area of Lead Sulfate.—The method of determining the surface area of the lead sulfate is that of Paneth and Vorwerk.³ The principle of the method was followed throughout, but it was necessary to modify it to some extent. The reference cited is lacking in detail on several important points. Inasmuch as the original dissertation of Vorwerk is not published in its entirety and is therefore not available to the American reader, the method as worked out by the authors is given in detail. The authors, however, claim originality only for such parts as deviate from, or are in addition to, those described in the reference cited above.

Theory of the Method.—For the theory of the method for determining the surface areas of lead precipitates, the reader is referred to the paper by Paneth and Vorwerk.

The Practical Manipulation.—A definite amount of lead sulfate (0.1 to 0.3 g.) was placed in a 50cc. Pyrex flask, to which was added 20 cc. of a radioactive saturated solution of lead sulfate. This solution was activated in the following manner. A piece of platinum foil 3.5 cm. on a side was attached to a piece of platinum wire and placed inside the tube containing a mixture of barium bromide and radiothorium,⁴ the platinum foil not being allowed to touch any of the material in the tube. The emanation was collected on the foil by connecting the latter for eight hours to the negative terminal of a 500-volt line. The foil was then immersed for 20 minutes in about 110 cc. of clear saturated solution of lead sulfate, after which it was removed and the solution allowed to stand for 15 minutes. Twenty cc. was then pipetted into each of five 50cc. flasks, three of which contained a known amount of dry lead sulfate, and two of which contained no sulfate.

In order to hasten the equilibrium between the thorium B in the solution and that on the surface of the lead sulfate, the flasks were placed in a shaking machine which shook them at 340 phases per minute, with an amplitude of 8 mm. The shaking was continued for one hour, which allowed a large margin above the time necessary to bring about equilibrium.

At the end of the shaking, the flasks were centrifuged for 30 minutes, and 5 cc. of the clear supernatant liquid was pipetted from each flask and placed in brass disks for evaporation. These disks were of such outside diameter that they would just fit into the lower chamber of the electroscope, so that all might be centered exactly to insure fair comparison. Each disk was hollowed out so as to form a basin which would hold 10 cc.

³ Paneth and Vorwerk, *Z. physik. Chem.*, **101**, 445 (1922).

⁴ Acknowledgment is made to Dr. H. N. McCoy of Chicago for the radiothorium.

as a maximum. The five disks, each containing 5 cc. of activated solution, were placed on a water-bath which had been carefully leveled, and the solutions were evaporated to dryness. When cool, the activities of the radioactive deposits on the disks were determined with a Lind α -ray electroscop.

The electroscop was carefully prepared to give accurate readings. Instead of the customary gold leaf, an aluminum leaf was used. By using a carefully selected piece of foil from which to cut the leaf and taking care not to fold or kink it in the cutting and mounting, it is possible to mount a leaf that will consistently pass over the scale with a uniform motion. A very fine thread of glass was attached to the lower end of the leaf to serve as an indicator on the scale.

The electroscop was charged by attaching one of the terminals of a 500 volt d. c. line to the charging terminal. This was much more satisfactory than using an ebonite rod for charging. Not only was it more convenient but the leaf could be brought to the same height on the scale each time.

In order to show more clearly the method of obtaining the surface area of the precipitate, the complete data and calculations are given for lead sulfate, Sample "B."

Flask No.	1	2	3	4	5
PbSO ₄ "B" g.	0.1000	0.1000	0.1000	none	none
Cc. of activated PbSO ₄ soln..	20	20	20	20	20
Time for leaf to pass over scale, seconds.....	32.0	31.7	32.1	22.9	22.9
	(a)	(b)	(c)	(d)	(e)
	32.2	31.9	32.1	22.9	..
	(i)	(h)	(g)	(f)	..
Av.	32.1	31.8	32.1	22.9	22.9

The readings for the activities of the deposits on the disks were taken in the alphabetical order indicated and then averaged, thus reducing to a minimum the error due to the decay of the radioactive material during the time required to take the readings. It would, of course, be somewhat more accurate to refer all the activities to any particular time chosen, by the use of the equation, $I_t = I_0 e^{-\lambda t}$, but for the purposes at hand, the first method is more direct and gives values well within the experimental errors.

The natural leak of the electroscop was 10 divisions in 42 minutes and 54 seconds, or 0.389 division per 100 seconds.

Av. activities for 1, 2 and 3: for 10 divisions	32 seconds	Av. activity for 4 and 5: for 10 divisions	22.9 seconds
	= 31.3 div. per 100 sec.		= 43.7 div. per 100 sec.
Natural leak	= 0.4	Natural leak	= 0.4
Actual activity	= 30.9	Actual activity	= 43.3
Activity adsorbed	= 43.3 - 30.9 = 12.4 div. per 100 sec.		

$$\text{Th B adsorbed} = \frac{12.4 \times 100}{43.3} = 28.7\%$$

$$\text{The specific surface} = \frac{\text{Th B ads. in } \%}{100 - \text{Th B ads. in } \%} \times \frac{\text{g. of Pb in soln.}}{a}$$

where a = the amount of lead sulfate in g. = 0.1000.

The number of grams of lead in solution was obtained by evaporating on a water-bath 100 cc. of solution saturated at 20°. Wt. of PbSO_4 per 100 cc. = 0.0043 g. = 0.00086 g. per 20 cc., which corresponds to 0.000561 g. of lead. The specific surface, expressed in grams of lead on the surface of 1 g. of lead sulfate = $\frac{28.7}{100 - 28.7} \times \frac{0.000585}{0.1000} = 0.002355$.

As a further check, the specific surface was determined by using 0.2 and 0.3 g. of lead sulfate. The net results of all determinations are given below in grams of lead on the surface of 1 g. of lead sulfate.

Determination 1 (Av. of 3), (0.1000 g. of PbSO_4) = 0.00235

2 (Av. of 2), (.2000 g. of PbSO_4) = .00239

3 (Av. of 2), (.3000 g. of PbSO_4) = .00244

Av. .00239

It now remains to calculate what this surface corresponds to in square centimeters.

If we consider one mole of lead sulfate (303.3 g.) in the form of a cube and take the density as 6.3, the volume of the cube is 48.1 cc., and the edge of the cube is 3.64 cm.

One mole of lead sulfate contains 6.06×10^{23} molecules, taking Millikan's value for Avogadro's number, from which we obtain 8.46×10^7 molecules on the edge of the cube or 1 molecule per 0.00042μ . One molecule then corresponds to a surface of $(0.00042\mu)^2$ or $1.85 \times 10^{-7}\mu$. Then the surface area of the lead sulfate = $1.85 \times 10^{-7}\mu \times$ (no. of molecules of lead sulfate on the surface).

The lead on the surface of 1 g. of the "B" sulfate equals 0.002396 g., which corresponds to 0.003507 g. of lead sulfate. The number of molecules on the surface of 1 g. can then be determined by the relation:

$$\frac{303.3}{(6.062 \times 10^{23})} = \frac{0.003507}{y}$$

whence $y = 70 \times 10^{17}$ molecules of lead sulfate on the surface of 1 g. of the precipitate. The surface area expressed in μ^2 = (no. of molecules of lead sulfate on the surface) \times (surface represented by 1 molecule of lead sulfate) = $(70 \times 10^{17}) \times (1.85 \times 10^{-7}) = 129 \times 10^{10}\mu^2$, which equals 12,900 sq. cm. per g.

The data for the various precipitates of lead sulfate used, together with their method of preparation and their surface areas expressed in square centimeters per gram are given below.

In the preparation of the precipitates of lead sulfate, doubly distilled water was used in the precipitation and for the washing. Each batch was washed repeatedly by decantation, using 3 liters of water each time. The precipitates were washed thrice after the wash water was neutral to methyl orange. The final wash water from each precipitate was used as the wetting liquid in the calorimetric determinations, in order to eliminate any heat effect due to solution. Inasmuch as this water had stood in

contact with the lead sulfate for at least 24 hours it was doubtless saturated.

PbSO₄ "A." 0.5 *N* sulfuric acid was added slowly at room temperature to 2.5 liters of a saturated solution of lead nitrate. Surface area, 5840 sq. cm. per g.

PbSO₄ "B." Prepared in the same manner as "A." Surface area, 12,900 sq. cm. per g.

PbSO₄ "C." 6 *N* sulfuric acid was added to 3 liters of a saturated solution of lead nitrate. Surface area, 13,700 sq. cm. per g.

PbSO₄ "D." 6 *N* sulfuric acid was added to a saturated solution of lead chloride. Surface area, 22,900 sq. cm. per g.

PbSO₄ "E." Prepared in the same manner as the "C" but the "fines" were decanted while still in suspension. Surface area, 9840 sq. cm. per g.

PbSO₄ "F." A saturated solution of lead nitrate and an equivalent amount of sulfuric acid in equal volume were poured together at 0° so as to meet in a common stream in order to obtain "volume condensation." Surface area, 15,800 sq. cm. per g.

PbSO₄ "G." The "fines" from "E." Surface area, 32,400 sq. cm. per g.

The Calorimeter.—An adiabatic calorimeter was used for making the calorimetric measurements.

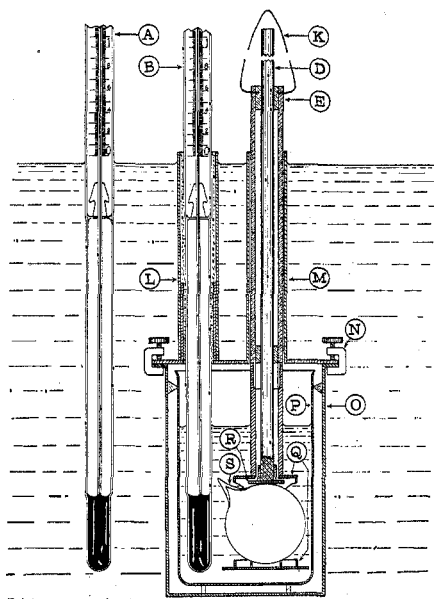


Fig. 2.

and was controlled by a hand switch. The cooling was obtained by running ice water into the bath. A stirrer in the outer bath was operated by a small motor. With careful attention it was possible to hold the temperature to within $\pm 0.001^\circ$.

The water equivalent was determined electrically. A small heater (not shown in the diagram) was connected to a storage battery in series

The calorimeter proper consisted of a "submarine" O (Fig. 2) in which was placed a silver plated copper can P. The bulb S containing the dried powder was held in a brass holder Q which was attached to a tubular piece of fiber E. The upper end of E hooked to a reciprocating rod above and was actuated by a motor at the rate of 54 strokes per minute. The holder Q, therefore, also served as a stirrer for the liquid in the calorimeter. An ebonite rod D containing a piece of metal R at its lower end served as a breaker for the bulb S. A standardized Beckmann thermometer B gave temperature readings inside the calorimeter. It passed through a "chimney" L in the cover of the calorimeter, the "chimney" being lined with cork in the lower end and cotton wool in the upper. A similar thermometer A gave temperature readings of the bath.

The outer bath of the calorimeter was heated by means of a resistance coil immersed directly in the water,

with a silver coulometer. The coulometer was prepared according to the method of T. W. Richards.⁵ A platinum dish of about 80cc. capacity served as cathode. The anode consisted of an electrolytic deposit of silver on a thin rod of c. p. silver. A porous porcelain cup was placed around the anode to prevent mechanically separated particles from falling into the dish. Voltage readings were made with a high resistance (13,000 ohms) voltmeter which was connected to the terminals of the heater through heavy copper leads, so that the resistance of the leads was negligible as compared with that of the heater. A variable resistance was placed in series with the heater and the battery so that the voltage could be kept constant throughout a determination. Just before closing the main switch in making a determination of the water equivalent, the terminals of the battery were connected to a resistance of the same magnitude as that of the heater in order to polarize the cells.

The bulb S containing a known weight of lead sulfate was placed overnight in the liquid with which it was to be wetted. The bulb was then placed in the holder and the calorimeter was assembled. The exact amount of water used as the wetting liquid was not determined, for instead of adding a definite amount of water each time, enough was added to bring the level to the same height for each run, so that the immersion of the thermometer B was the same in all determinations.

Instead of holding the outer bath at any particular temperature and waiting for the water in the calorimeter to come to the same temperature, it was found that thermal equilibrium could be brought about more easily by letting the two temperatures tend toward equilibrium for about an hour without any regulation. The thermometer B was then read and the outer bath brought to the same temperature, the two thermometers having been carefully calibrated against each other. By this method all determinations were not made at exactly the same temperature, but were between 19.5° and 21°. This procedure would not be legitimate in measuring heat effects of processes that had a temperature coefficient other than unity, but inasmuch as no heat effect was observed, this procedure resulted in no error.

After temperature equilibrium had been maintained for 30 minutes, the stirrup K was unhooked from the hanger above and the bulb S was broken by tapping on the crusher D. As soon as the bulb was broken, the stirrer D was worked up and down rapidly by hand for 15 seconds and then again hooked to the reciprocating rod above.

With lead sulfate in the bulbs, and using the final wash water from the precipitate as the wetting liquid, the rise of temperature was of the order of magnitude of 0.006° to 0.008°.

As soon as the temperatures as indicated by the two thermometers were

⁵ Richards and Heimrod, *Z. physik. Chem.*, 41, 302 (1902).

again in equilibrium, the water equivalent of the calorimeter and its contents was determined.

Results

Six experiments were conducted to determine the heat evolved due solely to the breaking of the bulb and to the stirring. In four of these the lead sulfate had been exposed for several days to air saturated with water vapor; in two, empty evacuated bulbs were used. The calories liberated varied by 0.088 between the maximum and minimum values, which shows that in all runs made under similar conditions, no significance can be attached to a variation of less than about 0.09 calorie.

In all the runs ice and salt were placed around the mercury trap J, except that carbon dioxide snow was used around the trap in four determinations, and liquid air was used in three determinations. All measurements on the heat of wetting were made between 19.5° and 21°, except that one was made at 0.2°.

Nineteen determinations were made on the heat of wetting. The total surface area of the lead sulfate used in any one determination varied between 76,000 and 530,000 sq. cm. The results of the tests are summarized in Table I. The first column of figures gives the results of the six runs mentioned above, in which empty evacuated bulbs were used as well as bulbs filled with lead sulfate saturated with water vapor to determine the heat liberated due to the impact of breaking and to the stirring. The next column shows the results of all the 19 determinations on the heat of wetting, while the last column shows the results of the same determinations but omitting three which varied considerably from the average in the amount of heat liberated. In one of these the high value was probably due to a heat effect due to solution, for the precipitate had been washed only six times and the wetting liquid was doubly distilled water instead of the final wash water as in the other runs. In the next run, conductivity water was also used, but the precipitate had been washed 14 times, with the result that the heat liberated was between the maximum and minimum

TABLE I
RESULTS

	Results of 6 prelim. determi- nations (No salt in bulb)	Results of 19 determi- nations on the heat of wetting	Results of 16 determi- nations on the heat of wetting
Max. temp. rise.....	0.008°	0.015°	...
Min. temp. rise.....	.004°	.005°	...
Av. temp. rise.....	.006°	.007°	...
Max. cal. liberated.....	.881	1.043	0.824
Min. cal. liberated.....	.790	0.792	.792
Av. cal. liberated.....	.818	.838	.812
Greatest dev. from av.....	+ .073	+ .205	- .020

shown in the last column. The high values in the other two determinations are unexplained. From this table it is evident that the heat of wetting of lead sulfate is zero, within the limit of experimental measurement.

Grateful acknowledgment is hereby made to Professor The Svedberg for his aid in the determination of the surface areas of the lead sulfate and for help in the solution of the problems involving radioactivity, as well as for many other helpful suggestions during seven months of the work.

Summary and Conclusions

An attempt was made to establish the relation between the heat of wetting of lead sulfate and its surface area. The surface areas of a number of samples of lead sulfate were determined by the use of a radioactive isotope of lead, thorium B, as indicator. The surface areas varied between 5840 and 32,400 sq. cm. per g. of the sulfate. The maximum surface of the total lead sulfate used in any one determination on the heat of wetting was 529,000 sq. cm. The value for the heat of wetting was zero within experimental error (0.09 cal.). This warrants the conclusion that the heat of wetting of lead sulfate when wetted with water saturated with lead sulfate is less than 0.09 cal. per 529,000 sq. cm., or less than 1.69×10^{-6} cal. per sq. cm. for lead sulfate that has been dried for 110 hours at a temperature of 224° and at a pressure of 0.005 bar.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY AND THE WESTERN ELECTRIC COMPANY, INCORPORATED]

PHOTOMICROGRAPHIC EVIDENCE OF THE CRYSTAL STRUCTURE OF PURE CERIUM

BY EARLE E. SCHUMACHER AND FRANCIS F. LUCAS

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A review of the literature reveals the fact that practically no reliable microscopic work has ever been done on the crystallographic properties of pure metallic cerium. There are two reasons for this: first, very little pure cerium has been isolated; and second, it is extremely difficult to prepare the specimens for microscopic examination because the metal oxidizes rapidly and thus is difficult to polish, and because it is violently attacked by practically all reagents which may be used for etching. This investigation was undertaken to secure information concerning the crystal structure of cerium, since some of this metal of a high degree of purity was available as a result of work recently carried on in this Laboratory.

Preparation of Pure Cerium

The cerium used in this study was prepared by electrolyzing some exceedingly pure cerium chloride. Both the anode and the electrolytic