be evaluated from the standard e. m. f. of the lead–lead sulfate electrode and the activity product, K, of lead sulfate by means of the relation

$$E^0_{\mathrm{Pb}} = E^0_{\mathrm{PbSO_4}} + (RT/2F) \ln K \qquad (1)$$

in which E^0_{Pb} is the standard e. m. f. of the lead electrode, $\mathrm{Pb/Pb^{++}}$ ($a = 1$), and $E^0_{\mathrm{PbSO_4}}$ is the standard e. m. f. of the lead–lead sulfate electrode, $\mathrm{Pb/PbSO_4(s), SO_4^{=}}$ ($a = 1$).

According to Harned and Hamer[9] the standard potential of the *two-phase lead amalgam*–lead sulfate electrode is 0.3495 v. at 25°. This is in agreement with the value 0.3505 v. given by Shrawder, Cowperthwaite, and La Mer.[10] We will use the average value 0.3500 ± 0.0005 v. Since the potential of two-phase lead amalgam against solid lead is 0.0058 v.,[3,5,6] the standard e. m. f. of the *solid lead*–lead sulfate electrode becomes 0.3558 v.

Kolthoff and von Fischer[11] recently have completed a study in this Laboratory of the *solubility* of lead sulfate by the conductance method and by direct analysis of the saturated solutions. From their data the solubility of lead sulfate at 25° is $1.48\ (\pm 0.02) \times 10^{-4}$ molar. This is in good agreement with the value 1.47×10^{-4} molar given by Crockford and Brawley,[12] and the value 1.48×10^{-4} molar taken from the data of Kolthoff and Rosenblum.[13]

The activity coefficient of lead sulfate in its saturated solution, computed from the Debye–Hückel limiting law, is 0.893. Using the extended Debye–Huckel equation, with the plausible value of 4 Å. for the ion-size parameter, the calculated activity coefficient is 0.897. From this value, and the value $1.48\ (\pm 0.02) \times 10^{-4}$ molar for the solubility of lead sulfate, the activity product of lead sulfate at 25° is $1.76\ (\pm 0.04) \times 10^{-8}$.

By substituting these data into eq. (1), we find for the standard e. m. f. of the *solid* lead electrode

$$E^0_{\mathrm{Pb}} = 0.3558 + \frac{0.05915}{2} \log (1.76 \times 10^{-8}) = 0.1264 \text{ v.} \qquad (2)$$

This value, computed from independent data of different investigators, is in excellent agreement with the value 0.1263 v. found by Carmody, and with the corrected values of Gerke (0.1264 v.) and Randall and Cann (0.1263). It is evident, therefore, that the present accepted[1] value of E^0_{Pb} (0.122 v.) is too low, and that the most reliable value is very close to 0.1263 v.

School of Chemistry of the
Institute of Technology
University of Minnesota
Minneapolis, Minnesota

Received December 30, 1937

---

(9) H. S. Harned and W. J. Hamer, This Journal, **57**, 33 (1935).

(10) J. Shrawder, Jr., I. A. Cowperthwaite, and V. K. La Mer, *ibid.*, **56**, 2348 (1934).

(11) Private communication, submitted to This Journal.

(12) H. D. Crockford and D. J. Brawley, *ibid.*, **56**, 2600 (1934).

(13) I. M. Kolthoff and C. Rosenblum, *ibid.*, **55**, 2656 (1933).

The Diazotization of Picramide

By Warren C. Lothrop

During further investigations of the coupling of 5-hydroxy-6-methylhydrindene[1] with diazotized amines it seemed of interest to use diazotized picramide. The diazonium solution obtained by the method recently described by de Milt and van Zandt,[2] however, gave no reaction and therefore their reported coupling with β-naphthol was repeated. The compound formed with this reagent had the properties ascribed to it by the authors: a relatively low melting point (147°), which, however, could be raised by repeated crystallization from acetic acid to 155°; remarkable solubility in common solvents, and, in addition, extreme solubility in cold dilute alkali. The latter seemed particularly significant since it was shown long ago[3] that azo compounds formed by the coupling of β-naphthol are usually insoluble in alkali.

The coupling of diazotized picramide with β-naphthol also has been reported by Schoutissen,[4] but the azo compound which this investigator obtained had properties very different from those given above. It melted at 260°, was insoluble in most common solvents, and dissolved in alkali only with decomposition.

It seemed possible that the product obtained by the newer method might in reality be the molecular addition compound previously prepared by Witt[5] and noted by Misslin.[6] This was found to be the case. A sample was prepared from equimolecular quantities of β-naphthol and picramide and analyzed: (calcd. for $\mathrm{C_{16}H_{12}O_7N_4}$: N, 15.05. Found: N, 14.67). This bright red compound (m. p. 161–162°) when mixed with the disputed product (m. p. 155°) melted at 155–157°, and was indistinguishable from it in other respects.

These results explain the observed discrepancy and lead to the conclusion that the new method outlined by de Milt and van Zandt for the di-

---

(1) Fieser and Lothrop, *ibid.*, **59**, 945 (1937).

(2) De Milt and van Zandt *ibid.*, **58**, 2044 (1936).

(3) Liebermann, *Ber.*, **16**, 2858 (1883).

(4) Schoutissen, This Journal, **55**, 4533 (1933).

(5) Witt, *Ber.*, **41**, 3093 (1908).

(6) Misslin, *Helv. Chim. Acta*, **3**, 636 (1920).

azotization of difficultly diazotizable amines is ineffective in the case of picramide.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

RECEIVED NOVEMBER 3, 1937

The Preparation and Purification of Hydrous Lanthanum Hydroxide Sols

BY THERALD MOELLER AND FRANCIS C. KRAUSKOPF

Although hydrous lanthanum hydroxide sols have been prepared by several workers,[1-5] the methods used are laborious or yield unstable suspensions. While attempting to improve upon some of these methods, it was noted that lanthanum hydroxide freshly precipitated in the presence of lanthanum chloride is readily peptized by the latter when the temperature is raised to 50°. The following procedure based upon this fact has been found convenient: 3.5 g. of lanthanum chloride heptahydrate is dissolved in a small amount of carbon dioxide-free water and from three-tenths to nine-tenths of the equivalent amount of normal ammonium hydroxide added. This gives a slimy, gelatinous precipitate. Sufficient carbon dioxide-free water is added to make a total volume of 400 cc., and the suspension is warmed to 50°. Peptization begins immediately, and within a few minutes the entire precipitate is dispersed to an homogeneous sol. The sol is cooled to room temperature, diluted to 500 cc., and dialyzed in collodion bags[6] stoppered to exclude air.

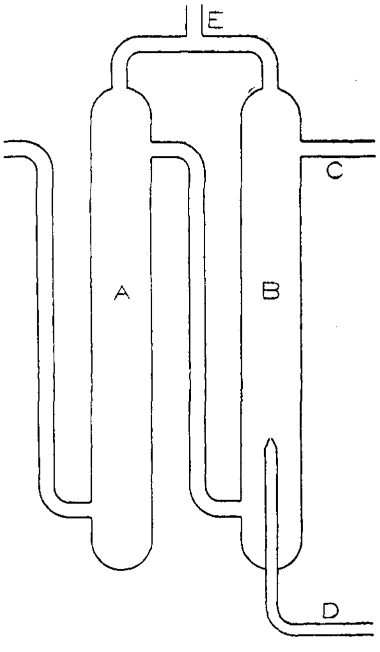

Fig. 1.—"Sweeping-out" apparatus.

In agreement with previous reports[7,8] concerning the relatively high basicity of lanthanum hydroxide and the ease with which its aqueous suspensions absorb carbon dioxide, it was found that dialysis against distilled water containing carbon dioxide converted the dispersed hydroxide into crystalline lanthanum carbonate. Accordingly, an apparatus was designed in which a continuous supply of carbon dioxide-free water was prepared by heating the water to 95° and sweeping out the residual gas with a current of nitrogen. The procedure is as follows: distilled water is heated by passing it through thirty feet (9.2 meters) of 10-mm. glass tubing immersed in an oil-bath maintained at 95 ± 1°. The hot water then enters the "sweeping-out" apparatus, the details of which are shown in Fig. 1. The two columns A and B are each 5 cm. in diameter and 40.5 cm. in height. The water enters at C and flows down column B countercurrent to a stream of nitrogen introduced at D. The exit gases are led off at E where a slight suction is maintained to ensure ready removal. From B the water flows into column A which serves to remove any entrained bubbles of gas not taken out in B. The exit water from A, after being cooled to any desired temperature in a countercurrent cooling system, flows into the dialyzer. The columns are supported in the oil-bath, and the nitrogen, after being passed over soda-lime, is preheated in a fifteen foot (4.6-meter) length of 8-mm. glass tubing before being passed into B. Pyrex glass is used throughout.

Sols dialyzed against water freed of its carbon dioxide in this apparatus are practically free from lanthanum carbonate. However, they readily absorb carbon dioxide from the air unless protected. Data for some of the dialyzed sols are given in Table I. It will be noted that all sols contain small amounts of chloride. Since attempts to remove the chloride completely by prolonged dialysis always have resulted in complete coagulation, it would appear that some lanthanum

---

(1) Böhm and Niclassen, *Z. anorg. Chem.*, **132**, 1 (1923); *cf.* Müller, *ibid.*, **57**, 311 (1908).

(2) Freundlich and Schalek, *Z. physik. Chem.*, **108**, 153 (1924).

(3) Britton, *J. Chem. Soc.*, **127**, 2142 (1925).

(4) Sadolin, *Z. anorg. Chem.*, **160**, 133 (1927).

(5) McCutcheon and Smith, THIS JOURNAL, **29**, 1460 (1907).

(6) Madson and Krauskopf, *J. Phys. Chem.*, **35**, 3237 (1931).

(7) Vesterberg, *Z. anorg. allgem. Chem.*, **94**, 371 (1916).

(8) Euler and Nilsson, *Ber.*, **57**, 217 (1924).