

Kendall and Fuchs' results and Taylor and Hulett's. This explanation is beside the mark. To us it seems fundamental to the theory of chemical statics that the true equilibrium point must be independent of the past thermal history of the system. Kendall and Fuchs' methods of preparing oxides by precipitation from solution and of preserving the oxides in an oven at 140° do not exclude the possibility of retention of minute traces of water vapor or the absorption of carbon dioxide. Exceedingly small quantities of either impurity may have been reversibly evolved and reabsorbed under the conditions of the experiments. Whatever may be the explanation of temperature reproduction obtained, it is obvious for reasons advanced herein that the temperatures observed were not true equilibrium temperatures for  $P_{O_2} = 1$  atmosphere for the systems studied. The rather revolutionary conclusions that in these cases equilibria have been shifted by catalysts are hardly justified.

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[CONTRIBUTION OF THE PHYSIOLOGICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

## THE ELECTROLYTIC PREPARATION OF CALCIUM AMALGAM

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The electrolytic method of preparing calcium amalgam has been very troublesome. The method of Kerp and Böttger<sup>1</sup> of having as the cathode a fine stream of mercury is complicated and time consuming and yields amalgams of very low calcium concentration. Smith and Bennett<sup>2</sup> simplified the method of preparation and obtained amalgams of higher concentration by electrolyzing in a beaker of 5.5cm. diameter, a layer of mercury on the bottom serving as cathode and a piece of platinum foil serving as the anode. They used at first saturated calcium chloride solution and then saturated calcium acetate solution. They were troubled, however, by the foaming of the solutions and discoloration because of the formation of a dark mixture of mercury and calcium hydroxide that apparently catalyzed the decomposition of the amalgam.

The following considerations led to the modification of the electrolytic method. While the calcium-ion concentration should be kept sufficiently high to have a minimum discharge of the hydrogen ion, the smaller the concentration of calcium ion, the less the chance of precipitation of calcium hydroxide which proved so troublesome to Smith and Bennett. The diffusion of calcium ion in the mercury is rather slow; moreover, according to Meyer<sup>3</sup> calcium lowers appreciably the surface tension of

<sup>1</sup> Kerp and Böttger, *Z. anorg. Chem.*, **17**, 300 (1898); **25**, 1 (1900).

<sup>2</sup> Smith and Bennett, *THIS JOURNAL*, **31**, 799 (1909); **32**, 622 (1910).

<sup>3</sup> Meyer, *Physik. Z.*, **12**, 975 (1911).

mercury, and the concentration of calcium would, therefore, tend to be greater at the interface. A large thin layer of mercury as the cathode is evidently preferable.

The procedure adopted was, therefore, as follows. A crystallizing dish about 25 cm. in diameter was used, presenting a surface 25 times as great as that used by Smith and Bennett.<sup>2</sup> The mercury serving as cathode on the bottom of the dish was of sufficient thickness only to cover the bottom, and the platinum wire that connected to the negative pole of the current was laid flat on the bottom. The anode, at which chlorine was given off, was a piece of platinum foil ( $2 \times 4$  cm.), parallel to and about 4 cm. above the mercury surface, and just under the surface of the solution. A solution of 1.75 *M* calcium chloride was found most satisfactory. The current used was 3.5 amperes. This arrangement prevented foaming or darkening of the solution even after an hour, and there was no appreciable heating of the solution (as found by other experimenters), owing to the larger cross-section and, therefore, smaller resistance of the solution. In a few instances there were noted centers of decomposition on the amalgam where hydrogen would be evolved, but by taking the drop off with a glass spatula the trouble could be obviated. After about a half hour a generation of hydrogen set in at various points of the amalgam, but even after this time the solution was still clear, neutral to litmus paper, and upon fortifying with concentrated calcium chloride solution the electrolysis solution could be used again. The amalgams obtained contained 0.069% to 0.075% of calcium, and the current efficiency was about 65%. Currents of 4 to 6 volts were found satisfactory, but at higher voltages some of the black mixture was formed which would cause decomposition. In a few cases the calcium chloride solution had a distinct odor of chlorine after the electrolysis, and it was found necessary to boil this solution and to treat it with hydrogen peroxide, and to neutralize the acidity with calcium hydroxide before it could be used again.

Merely washing the amalgam with water, after the electrolyzing solution was poured off, was found to be insufficient in a number of cases. The amalgam when dry was extremely sensitive to even traces of air, and in a few minutes a scum formed and the amalgam decreased in strength very quickly. It was found, however, that by letting the amalgam drop in a fine spray into a 2-liter bottle filled with distilled water it was much less subject to oxidation. To keep the amalgam it has been found satisfactory to fill a flask with carbon dioxide by displacement, pour the amalgam into it very quickly without taking any precautions to keep the air away, remove the water with filter paper, pass in carbon dioxide for several minutes and stopper the flask. The amalgam remained fairly clear, although there was undoubtedly some air left in the flask.

It is possible that during the electrolysis there are formed on the large cathode surface small quantities of compounds containing calcium in a degree of oxidation intermediate between the ionic and metallic states, compounds of the type of  $\text{CaCl}$ , which was found by Borchers and Stockem<sup>4</sup> during the electrolysis of calcium chloride. An easily oxidized compound of this character would catalyze oxidations of other substances in like manner to that found by Dhar<sup>5</sup> in a number of catalyzed oxidations. Calcium amalgams prepared in this manner and diluted with mercury were found satisfactory for measuring the potentials of calcium amalgams against aqueous solutions of calcium salts.

### Summary

An improved method for the electrolytic preparation of calcium amalgam has been presented.

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## THE CATALYTIC DECOMPOSITION OF CERTAIN OXIDES

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In our article against which Taylor and Hulett<sup>1</sup> have raised certain objections it was noted that the aim of the work was to secure a preliminary survey over a comparatively wide field rather than to obtain results of the highest accuracy for a few isolated systems. Some of the more interesting systems are now being examined in greater detail by more refined methods, and a full reply to Taylor and Hulett's criticisms must be postponed until additional experimental work bearing directly upon the several points at issue is completed. In view of the fundamental character of their criticisms, however, a brief statement as to how far we consider our conclusions to be affected thereby becomes immediately necessary.

**Silver Oxide.**—As reference to the context will show, the agreement of our results with those of Lewis was intended to refer to the change in rate of decomposition with time of heating not to decomposition temperatures at one atmosphere pressure. In point of fact, extrapolation of the measurements of Lewis, carried out between  $302^\circ$  and  $445^\circ$ , down to  $185^\circ$  is legitimate only if no allotropic changes take place within the temperature interval involved, and from the work of Kohlschütter and Eydmann<sup>2</sup> it appears that silver undergoes a transition at about  $260\text{--}270^\circ$ . It is true that the results of Lewis have been extrapolated down

<sup>4</sup> Borchers and Stockem, *Z. Elektrochem.*, **8**, 757 (1902).

<sup>5</sup> Dhar, *Proc. Acad. Sci. Amsterdam*, **23**, 1074 (1921).

<sup>1</sup> Taylor and Hulett, *THIS JOURNAL*, **44**, 1443 (1922).

<sup>2</sup> Kohlschütter and Eydmann, *Ann.*, **398**, 7 (1913).