

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 CaCl , which was found by Borchers and Stockem⁴ 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 Dhar⁵ 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.

BALTIMORE, MARYLAND

THE CATALYTIC DECOMPOSITION OF CERTAIN OXIDES

BY JAMES KENDALL AND FRANCIS J. FUCHS

Received March 13, 1922

In our article against which Taylor and Hulett¹ 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° and 445° , down to 185° is legitimate only if no allotropic changes take place within the temperature interval involved, and from the work of Kohlschütter and Eydmann² it appears that silver undergoes a transition at about 260 – 270° . It is true that the results of Lewis have been extrapolated down

⁴ Borchers and Stockem, *Z. Elektrochem.*, **8**, 757 (1902).

⁵ Dhar, *Proc. Acad. Sci. Amsterdam*, **23**, 1074 (1921).

¹ Taylor and Hulett, *THIS JOURNAL*, **44**, 1443 (1922).

² Kohlschütter and Eydmann, *Ann.*, **398**, 7 (1913).

to 25° to obtain values for the free energy of formation of water and the voltage of the hydrogen-oxygen cell which are concordant with those derived from other and independent data, but the recent observation of Rördam³ that silver oxide also undergoes transition at 132° suggests that this concordance is possibly due to the counterbalancing effect of two disturbing factors. In any case, the fact that Kohlschütter and Eydmann found some absorption of oxygen by silver to occur at 270° under 1 atmosphere pressure would seem to indicate that the equilibrium pressure of 7 atmospheres at 254° calculated by Taylor and Hulett is considerably in error.

Mercuric Oxide.—The validity of Taylor and Hulett's criticisms upon this section of our work is freely admitted. Our apparatus, as employed, could not give equilibrium temperatures for $p_{O_2} = 1$ atmosphere, and a repetition of our measurements with a properly modified technique is obviously requisite before any strict comparison with the results of Taylor and Hulett can be made. If we assume, however, that the partial pressure of oxygen in the vapor just above the dissociating oxide in our experiments was $\frac{1}{3}$ of an atmosphere (which must, approximately, have been the case), it is interesting to note that our decomposition temperature, 431°, is in very fair agreement with that obtained under the same conditions by interpolation from the curve of Taylor and Hulett, near 445°. The discrepancy of over 60° previously indicated is therefore largely removed. A satisfactory explanation of the larger divergencies apparent in systems containing added oxides, however, is still lacking.

Barium Peroxide.—There is no evidence at all that barium peroxide and barium monoxide form solid solutions with each other at the temperature of our experiments (300–350°). Hildebrand did conclude, from measurements at a much higher range (700–800°), that solid solutions existed, but Lewis and Randall⁴ have pointed out that an inspection of his curves makes it seem equally probable that barium hydroxide was largely responsible for the phenomena which he attributed to solid solution, and that in his univariant system the two oxides behave as nearly pure substances. Even if some mutual solubility could be definitely established between 700° and 800°, it would presumably diminish rapidly as the temperature is lowered. We hope to present conclusive evidence as to the essentially univariant and reversible character of the equilibrium in the presence of foreign oxides in a later communication.

NEW YORK, N. Y.

³ Rördam, *Z. physik. Chem.*, **99**, 474 (1921).

⁴ Lewis and Randall, *THIS JOURNAL*, **36**, 1986 (1914).