# THE CATALYTIC DECOMPOSITION OF CERTAIN OXIDES

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In a recent article Kendall and Fuchs[1] reported measurements of the temperatures at which certain oxide mixtures were in "equilibrium" with oxygen at a pressure of one atmosphere. They find that certain oxides, when mixed with silver oxide, mercuric oxide, or barium peroxide, lower this "equilibrium temperature." In other words, in these cases we have equilibrium definitely shifted by catalysts.

Kendall and Fuchs' interpretation of their results may be seriously questioned. A pure oxide dissociating into non-volatile metal and oxygen is a system of two components and three phases, and therefore possesses one degree of freedom. At any fixed temperature there is a corresponding equilibrium pressure of oxygen. Such a system is $Ag_2O:Ag:O_2$ and probably $BaO_2:BaO:O_2$. A pure oxide dissociating into two gases is a system of two components and two phases and therefore possesses two degrees of freedom. Such a system is $HgO:Hg:O_2$. To speak in this case of an equilibrium pressure of oxygen at any fixed temperature without specifying the corresponding partial pressure of mercury vapor is inadmissable.

**Silver Oxide.**—Kendall and Fuchs find for pure silver oxide an oxygen equilibrium pressure of one atmosphere at 254°. This result is said to be in agreement with the measurements of G. N. Lewis.[2] Calculations from Lewis'[3] formula give 7 atmospheres for 254° and for 1 atmosphere 185°. From this it appears that the data of Kendall and Fuchs are some 70° higher than those of Lewis. In no instance did a catalyst lower the equilibrium temperature below the Lewis value of 185°. Upon what ground Kendall and Fuchs consider their results in agreement with Lewis requires explanation.

**Mercuric Oxide.**—Mercuric oxide when heated dissociates according to the following equation

$$HgO\ (\text{solid}) \rightleftarrows 2Hg\ (\text{gas}) + O_2\ (\text{gas})$$

The complete mathematical expression for the equilibrium is

$$K = \frac{p_{Hg}^2 \, . \, p_{O_2}}{p_{HgO}}$$

where $K$ is the equilibrium constant. The partial pressure of mercuric oxide is obviously constant and practically of a negligible order of magnitude, so that the expression may be simplified by writing $K = p_{Hg}^2 \times p_{O_2}$. Theoretically no pressure of oxygen, however great, can be in equilibrium with mercuric oxide in the complete absence of mercury vapor. Kendall and Fuchs' method of measurement could yield correct results

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[1] Kendall and Fuchs, This Journal, **43,** 2017 (1921).

[2] Ref. 1, p. 2022.

[3] Lewis, This Journal, **28,** 139 (1906).

for $P_{O_2}$ = 1 atmosphere only if the value of the equilibrium constant $K$ happened to be such that the partial pressure of mercury vapor is negligible at a total equilibrium pressure of one atmosphere. No evidence is brought forward that this is the case. Taylor and Hulett's[4] results indicate a value of $P_{O_2}$ = 1 atm. at 495° when $P_{Hg}$ = 2 atmospheres. Obviously this temperature cannot be compared with Kendall and Fuchs' temperature of 431° for "$P_{O_2}$ = 1 atm." when $P_{Hg}$ is undetermined. Taylor and Hulett's results are checked by the heat of formation of mercuric oxide determined by thermal methods. Both static and dynamic methods checked. Iron oxide, cadmium oxide and manganese dioxide accelerated the decomposition rate, but none effected any change in the equilibrium pressure.

The use which has been made[5] of the data of Taylor and Hulett on the dissociation of mercuric oxide and of Lewis on the corresponding dissociation of silver oxide for the thermodynamic calculation of the free energy of formation of water or of the voltage of the hydrogen-oxygen cell serves also as a check on the correctness of these two sets of measurements. The calculations from the two researches yield concordant values. The independence of the two sets of data is a double check on their validity.

**Barium Peroxide.**—Hildebrand[6] found the dissociation of barium peroxide extremely slow, and that traces of water were necessary to cause it to dissociate at all. When the ratio of barium peroxide to barium oxide was large, the system was divariant. This he attributed to formation of solid solutions, but Lewis and Randall[5] have pointed out that since water was present, barium hydroxide also must have been present and that the $BaO_2:BaO:O_2$ system is probably monovariant. Kendall and Fuchs' method of preserving their material does not exclude the possibility of the presence of barium hydroxide, and this impurity could easily account for the extraordinary lowering of the equilibrium temperature. It is certainly not permissible to compare their results with Hildebrand's value without examining the nature of the solid phases present in Kendall and Fuchs' oxide mixtures. Hedvall's[7] heating curves of mixed oxides containing barium peroxide certainly point to oxygen evolution at comparatively low temperatures, but there is no evidence presented in his work that these effects are reversible.

Kendall and Fuchs base their entire argument on the experimental fact that the same reproducible temperatures were obtained upon heating and cooling. In the case of mercuric oxide they advance the explanation of different modes of preparation to account for the discrepancy between

[4] Taylor and Hulett, *J. Phys. Chem.*, **17**, 565 (1913).

[5] Lewis and Randall, *ibid.*, **36**, 1983 (1914).

[6] Hildebrand, *ibid.*, **34**, 246 (1912).

[7] Hedvall, *Z. anorg. Chem.*, **108**, 119 (1919).

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[1] 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[2] 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[3] calcium lowers appreciably the surface tension of

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[1] Kerp and Böttger, *Z. anorg. Chem.*, **17**, 300 (1898); **25**, 1 (1900).

[2] Smith and Bennett, THIS JOURNAL, **31**, 799 (1909); **32**, 622 (1910).

[3] Meyer, *Physik. Z.*, **12**, 975 (1911).