Summary

A new method of determining the melting points of certain oxides is described. The melting point of calcium oxide by this method was determined to be 2849°K., which is in good agreement with the generally accepted value 2843°K. determined in a different way by Kanolt. Similarly, the melting points of barium oxide and strontium oxide were found to be 2196°K. and 2703°K., respectively.

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NOTE

The Catalytic Decomposition of Hydrogen Peroxide in an Acid Chlorine-Chloride Solution.—Since the publication of our paper on the catalytic decomposition of hydrogen peroxide in an acid chlorine-chloride solution,[1] Mr. E. A. Guggenheim of Cambridge University has directed our attention to the fact that our derivation of Equation 33 (by means of which we computed the time required for the chlorine concentration to reach some definite fraction of its steady-state value) involves an error in logic. We obtained Equation 33 by combining Equation 31, which is quite correct, with Equation 32; but Equation 32 is incorrect, since it was obtained by integrating, between the limits $t = 0$ and $t = t$, the steady-state rate equation (No. 3) which does not fit the initial rate within 100%. However, a relation between the time and the ratio of the chlorine concentration to its steady-state value can be readily obtained in the following manner.

Since the concentrations of the chloride and hydrogen ions are assumed to be constant during any one experiment,[2] we may combine Equations 18, 19, 21, 22 and 26 with the steady-state relation $K_1/K_2 = y_s[H^+]^2[\mathrm{Cl}^-]^2$, and obtain the following equation.

$$\mathrm{d}y/\mathrm{d}t = K_1[\mathrm{H_2O_2}]\ [\mathrm{H}^+]\ [\mathrm{Cl}^-]\ (1 - y/y_s) \qquad \mathrm{A}$$

By means of Equation 31, $[\mathrm{H_2O_2}]$ may be expressed as a function of y,

$$[\mathrm{H_2O_2}] = [\mathrm{H_2O_2}]_0 - 2\,y_s\,ln(y_s/(y_s - y)) + y \qquad \mathrm{B}$$

where the last term, y (or ay_s), is negligibly small in comparison with the rest of the expression. Substituting in Equation A we obtain the following relation.

$$\frac{\mathrm{d}y}{\mathrm{d}t} = K_1\ [\mathrm{H_2O_2}]_0\ [\mathrm{H}^+]\ [\mathrm{Cl}^-]\ \frac{y_s - y}{y_s}\left(1 - \frac{2\,y_s}{[\mathrm{H_2O_2}]_0}\,ln\,\frac{y_s}{y_s - y}\right) \qquad \mathrm{C}$$

By integration between $y = 0$ and $y = ay_s$, and replacing $2\,K_1$ by K, we find,

$$t = -\frac{1}{K\ [\mathrm{H}^+]\ [\mathrm{Cl}^-]}\,ln\left(1 - \frac{2\,y_s}{[\mathrm{H_2O_2}]_0}\,ln\left(\frac{1}{1 - a}\right)\right) \qquad \mathrm{D}$$

Using this equation we may repeat the computations given on p. 2081

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[1] Livingston and Bray, This Journal, **47,** 2069 (1925).

[2] See Ref. 1, p. 2080, lines 6–10.

of our paper. For Expt. 17, Table I (see also No. 2, Table III), we find that the time intervals corresponding to values of a of 0.75, 0.99 and $(1 - 10^{-10})$ are 0.44, 1.44 and 7.3 minutes, respectively. For Expt. 5, Table III, the time required for y to reach a value of 0.99 y_s is 17 minutes when K and $[H_2O_2]_0$ are assumed to be 3.0×10^{-4} and 0.20, respectively. These new results do not affect any of the conclusions which we have already presented.

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SYNTHESIS AND PROPERTIES OF 3-CHLORO-DIACETONE-GLUCOSE

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The work of Freudenberg[1] and his students has emphasized the value of the diacetone hexoses in the preparation of definite mono-derivatives of the hexoses. The 3-chloro-diacetone-glucose was desired for the preparation of carbon-phosphorus and carbon-arsenic derivatives for biological purposes. It seemed probable that availability of this chlorine derivative would also make possible the synthesis of many other glucose derivatives not feasible from the diacetone-glucose itself.

The 3-chloro-diacetone-glucose has been obtained but its stability will preclude its use as a synthetic agent to any extent; however, in both the corresponding bromine and iodine derivatives the halogen atom should prove sufficiently labile for such work. Incidentally, the chlorination with phosphorus pentachloride has yielded phosphorus derivatives of diacetone-glucose not easily hydrolyzed, which are being further investigated.

The preparation of these derivatives depends upon the "non-acid nature" of hydrogen chloride in anhydrous petroleum ether. By operating in carefully purified petroleum ether over freshly ignited sodium carbonate, diacetone-glucose has been successfully treated with phosphorus pentachloride, trichloride, oxychloride and thionyl chloride, hydrogen chloride being evolved in all cases. The merest trace of moisture causes hydrolysis of the acetone groups from the glucose molecule with complete loss of the derivatives sought. The following chart shows the general course of the reactions, the 3-chloro-diacetone-glucose, the bis(diacetone-glucose) sulfite ester and the diacetone-glucose sulfonate of diacetone-glucose being the only products so far examined in detail.

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[1] Freudenberg and students, *Ber.*, (a) **55,** 929; (b) 3233, 3239 (1922); (c) **56,** 1243; (d) 2119 (1923); (e) **58,** 294; (f) 300 (1925).