and the filtrates and precipitates were analyzed for total cobalt and for radioactive cobalt by use of a Geiger counter.

Tests for exchange in the absence of peroxide were made by the same scheme, omitting the addition of peroxide to the cross-mixed solutions. The solutions were allowed to stand for twenty-four hours before filtration and analysis.

Results and Discussion

The results are given in Table I as total cobalt content and radioactivity of the solid and soluble phases, before and after the period in which exchange could have occurred. Material balances on total cobalt and total radioactivity close to within 5%. It is evident that very little exchange takes place in the twenty-four hour period and that hydrogen peroxide has no tendency to accelerate it. It is believed that the slight exchange indicated could be the result of adsorption of salts on the colloid and failure of the filter to remove the colloid completely.

TABLE I

EXCHANGE BETWEEN Co^{++} AND $Co(OH)_3$

Sample	Mg. Co	C. p. m./mg. Co	C. p. m./mg. Co for complete exchange
	A. In presence of H_2O_2		
F_1	41.6	0	..
P_3*	45.8	46.5	..
F_1'	42.2	3.1	24.4
P_3*'	44.7	45.3	24.4
F_4*	40.2	40.6	..
P_2	47.8	0	..
F_4*'	38.6	41.9	18.6
P_2'	43.6	2.3	18.6
	B. In absence of H_2O_2		
F_1	44.7	0	..
P_3*	44.7	49.0	..
F_1'	42.2	4.5	24.5
P_3*'	43.6	44.3	24.5
F_4*	40.2	46.2	..
P_2	43.1	0	..
F_4*'	41.0	38.8	22.4
P_2'	42.2	6.0	22.4

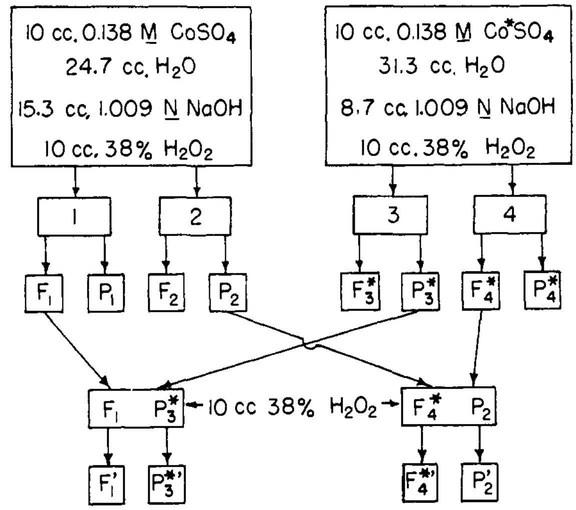

Fig. 1.

Acknowledgment.—The authors are indebted to the Naval Bureau of Ordnance for support of and permission to publish this work.

Summary

The extent of exchange between cobaltous ion and colloidal cobaltic hydroxide in water has been determined in both the presence and absence of hydrogen peroxide, by the use of a radioactive cobalt tracer. Within the accuracy of the methods, practically no exchange occurs in either case over a twenty-four-hour period.

RECEIVED FEBRUARY 3, 1949

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Investigations of Galvanic Cells with Solid and Molten Electrolytes[1]

BY WALTER J. HAMER AND JOHN P. SCHRODT

Numerous investigations have been made of reversible cells with molten electrolytes.[2] For the most part these studies were made for the purpose of obtaining thermodynamic data on metallic solutions or molten salts and were conducted at temperatures at which all or part of the cell components were in the molten state. Few data, however, are available on cells of this type below the melting point of the electrolyte, on their characteristics in the inactive solid state, or on their discharge characteristics when there is a net flow of electric current.

Jacques,[3] Reed,[4] Baur[5] and Haber[6] and their

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[1] Presented at the Symposium on Galvanic Cells and Batteries before the Division of Physical and Inorganic Chemistry of the American Chemical Society, April 19, 1948.

[2] N. W. Taylor, THIS JOURNAL, **45**, 2865 (1923); E. J. Salstrom, T. J. Kew and T. M. Powell, *ibid.*, **58**, 1848 (1936); J. H. Hildebrand, "Solubility of Non-electrolytes," Reinhold Publ. Corp., 2nd ed., New York, N. Y., 1936, Chap. XI; C. Wagner and G. Engelhardt, *Z. physik. Chem.*, **159A**, 241 (1932); H. Seltz, *Trans. Electrochem. Soc.*, **77**, 219 (1940); J. A. Yanko, A. E. Drake and F. Hovorka, *ibid.*, **89**, 357 (1946).

[3] W. W. Jacques, *The Electrician*, **36**, 768 (1896).

[4] C. J. Reed, *J. Franklin Institute*, **142**, 1 (1896).

[5] E. Baur, *Z. Elektrochem.*, **16**, 300 (1910); E. Baur and H. Ehrenberg, *ibid.*, **18**, 1002 (1912); E. Baur, A. Petersen and G. Füllemann, *ibid.*, **22**, 409 (1916); E. Baur, W. D. Treadwell and G. Trümpler, *ibid.*, **27**, 199 (1921).

[6] F. Haber and L. Bruner, *Z. Elektrochem.*, **10**, 697 (1904); F. Haber and A. Moser, *ibid.*, **11**, 593 (1905); F. Haber, *Z. anorg. Chem.*, **51**, 245 (1906); F. Haber and G. W. A. Foster, *ibid.*, **51**, 289 (1906).

associates and others[7] have investigated cells with molten electrolytes as potential sources of electrical energy. However, these cells involved gaseous electrodes and therefore were inconvenient for many purposes. More important, they were either readily polarized or had low voltages, and in many cases the reactions of the cells were largely chemical rather than electrochemical. Gyuris[8] proposed a cell with an electrolyte of molten sodium nitrate which did not utilize a gaseous oxidizing agent. Manganese dioxide was used for this purpose and molten sodium was used for the other electrode. The cell operates at 450°. Molten sodium is very reactive and special means must be taken to prevent it from diffusing to the manganese dioxide electrode.

Cells with molten electrolytes must, of course, be heated but the electrical energy is not obtained from heat energy but from the chemical processes that occur at the high temperatures. A number of attempts have been made to convert heat energy directly to electrical energy using thermopiles,[9] but the e.m.f. of a single couple is always small, thermopiles deteriorate rapidly, and their efficiency cannot exceed the thermodynamic efficiency or is limited by the fact that the heat absorbed at the hot junction cannot be totally transformed to electrical energy.

Galvanic cells with solid-molten electrolytes may be very suitable for reserve-type cells that may be activated by heat and thereby supplement those reserve-type cells that are activated by water,[10] by shock[11] or by other mechanical means.[11] Furthermore, the activation period for these cells should be relatively short.

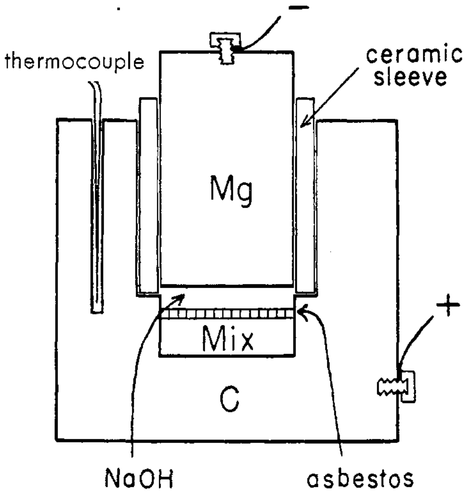

Fig. 1.—Schematic diagram of experimental cell for studies of cells with molten electrolytes (design no. 1).

It is the purpose of this paper to present data on miniature cells with molten or solid electrolytes over a wide range of temperature extending from room temperature (25°) to and above the melting point of the electrolytes, to show the feasibility of activation of cells by heat, to determine the differences in the characteristics of cells in the inactive (solid) and active (molten) states, and to ascertain if cells with molten electrolytes show properties similar to those of the usual primary cells. It is well known that inorganic substances generally have low conductivity in the solid dry state but when molten have conductivities exceeding the conductivities of the same substance in aqueous solution. Therefore, cells should differ considerably in their properties when the electrolyte is solid or fused, and should be activated by heat with short activation periods at the instant of fusion of the electrolyte. Data are also included to show the effect of temperature and discharges on low current drains on the voltages of miniature cells in the molten state.

Experimental

The cell investigated may be represented by

Mg: solid or molten electrolyte: MnO_2: C.

Manganese dioxide ore (Gold Coast African ore containing 87.5% manganese dioxide) was used as the active oxidizing agent. Manganese dioxide ore, however, is a poor electronic conductor and was mixed, therefore, with Shawinigan black (acetylene black) in the ratio of 85 parts manganese dioxide ore to 15 parts black. Several electrolytes of relatively low melting points were studied; only those electrolytes were used that melt below the melting point of magnesium (651°) and the decomposition point of manganese dioxide (535°).

The cell design is shown schematically in Figure 1. A "mix" of 0.85 g. of manganese dioxide ore and 0.15 g. of black was placed in a reservoir, 0.25″ deep and 0.375″ in diameter, in a carbon block, 1.125″ high and 1.5″ in diameter. A thin strip of soft asbestos (0.2 mm. thick) was placed above the mix to prevent diffusion of the mix into the molten electrolyte. The electrolyte was then packed as the dry salt or poured, when molten, over the asbestos. A magnesium rod, 0.5625″ in diameter and 1.3125″ long, was then inserted to a depth of 0.4375″ so that the rod and the mix covered with asbestos were separated by 2 mm. All parts were machined to fit snugly. Other details are shown in the figure. A second design was also used. It differed from the first design only in that a carbon rod was used in place of the magne-

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[7] A. J. Allmand and H. J. T. Ellingham, "The Principles of Applied Electrochemistry," Longmans, Green & Co., New York, N. Y., 1924, Chap. XIII.

[8] J. Gyuris U. S. Patent 2,081,926, June 1, 1937; 2,102,701, Dec. 21, 1937.

[9] W. R. Cooper, "Primary Batteries," The Electrician Printing and Publ. Co., Lt., Salisbury Court, E. C., 1901, Chap. VI.

[10] J. B. Mullin and P. L. Howard, *Trans. Electrochem. Soc.*, **90**, 529 (1946).

[11] J. P. Schrodt, W. J. Otting, J. O. Schoegler and D. N. Craig, *ibid.*, **90**, 405 (1946).

sium rod and a magnesium disk, 0.25″ thick, was joined at the lower end of the carbon rod.

The cell was heated either in an electrically controlled oven or by a gas burner, at first rapidly and then slowly at a rate of about 0.1° per minute as the melting point of the electrolyte was approached in order to determine the activation time of the cell. The temperature of the cell was determined with a calibrated copper–constantan thermocouple.

The open-[12] and closed-circuit voltages of the cells were determined at frequent intervals (every one or one-half minute) with a 20,000-ohm voltmeter (10,000 ohms per volt). The closed-circuit voltages were measured when a resistance of 100, 50, 25 or 10 ohms was across the terminals of the cell. Low rates of discharge were necessary because of the small size of the experimental cell. For illustration of the principles involved only the data obtained with the 100-ohm resistance are given for the cells in the solid state. Under these conditions the current density is of minor importance.

Results

Data obtained with sodium hydroxide are given in Fig. 2. At room temperature the cell had zero open- and closed-circuit voltages. As the temperature of the cell was increased, the open-circuit voltage increased reaching a maximum value after the melting point of the alkali was reached and exceeded. In this case little or no current is drawn from the cell. On the other hand, the cell gave no closed-circuit voltages until a temperature of about 250° was reached and no sustained voltages until the melting point of the alkali (318.4°) was reached or exceeded. Therefore, little or no current was drawn from the cell until the electrolyte became molten. This was also true for external resistances less than 100 ohms.

In this experiment the open-circuit voltages exhibited an initial peak at about 130° (188.4° below the melting point of sodium hydroxide). This peak may be attributed to traces of water in the alkali which contributes to the conductivity of the alkali, the mobility of the ions, and hence to the voltage of the cell. As the water was eliminated by the heat the open-circuit voltage fell, passed through a minimum, and then increased with rise in temperature. That this peak was caused by the presence of traces of water was shown in two ways. On cooling the cell after the alkali had become molten and kept in this state for about an hour, the open-circuit voltages did not exhibit this peak. Furthermore, a cell in which precautions were taken to eliminate water as far as possible did not exhibit this initial peak in voltage prior to the melting of the alkali (Fig. 3). In this experiment the carbon block, magnesium rod, and the mix were dried in a desiccator at 110° for several days and heated to 300° for about thirty minutes before the cell was assembled. The alkali was fused and boiled for about thirty minutes before added to the cell. The assembled cell was then cooled in a desiccator for an hour before measurements of voltage were made.

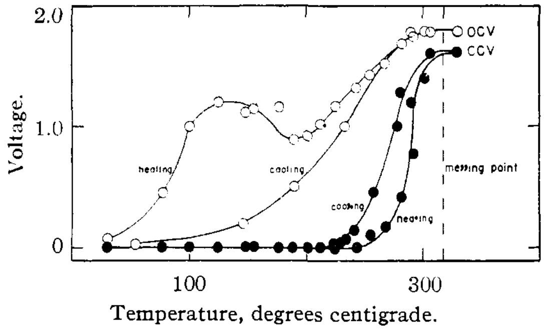

Fig. 2.—Open- and closed-circuit voltages of the cell Mg: molten NaOH: MnO_2: C as a function of temperature in degrees centigrade, when the alkali is dry and when it contains traces of moisture.

The voltages obtained on heating and cooling (Fig. 2) did not coincide, owing to the presence of water during the heating and to the fact that molten alkali adheres to the electrodes better than does solid alkali. The cells did not give sustained voltages until after the melting point of the alkali was exceeded because of the time required for the diffusion of the molten ions, of the time required for temperature equilibrium within the cell, and because the alkali does not all become molten as soon as the melting point of the electrolyte is attained. However, the activation time for sustained voltages is of the order of a few seconds providing the melting point of the alkali is exceeded by a few degrees.

In Fig. 3, the voltages as determined with a potentiometer, an electrometer (11,000,000 ohms) and a voltmeter (20,000 ohms) are also given as a

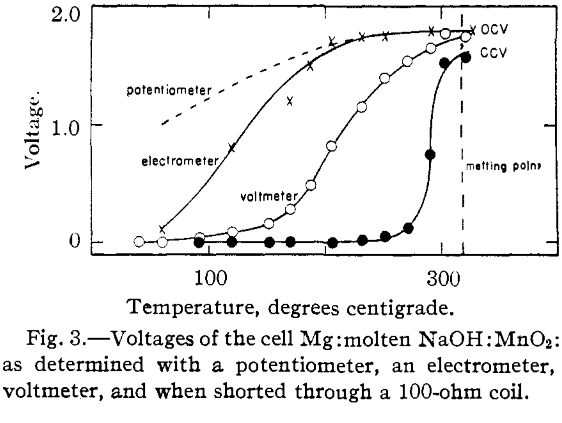

Fig. 3.—Voltages of the cell Mg: molten NaOH: MnO_2: C as determined with a potentiometer, an electrometer, a voltmeter, and when shorted through a 100-ohm coil.

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[12] The term open-circuit voltage is frequently used in connection with the testing and specifications of dry cells and batteries. The open-circuit voltage is usually measured with a voltmeter of designated resistance and may or may not be equal to the e. m. f. of the cell depending on the resistance of the meter and the internal resistance of the solid cell or the "irreversible effects" of the molten cell. In the present case, the open-circuit voltage is not equivalent to the e. m. f. of the cell, as is shown later.

function of temperature. The voltages depend on the amount of current drawn from the cell and are distinctly different when the electrolyte is in the dry solid state but approach the same value as the electrolyte becomes molten. The data obtained by the potentiometer are given as a dotted line because the internal resistance of the solid cell was so great as to make the actual values somewhat uncertain. The differences in voltages as determined by the three instruments show that the internal resistance of the cell is very high when the electrolyte is solid and decreases with rise in temperature of the cell.

Although solids of highly electropositive elements have low conductivity when in the dry solid state, Lorenz and his associates[13] have shown that they do conduct electric current to some extent and that this ability increases exponentially with increases in temperature according to the Kohlrausch equation. This ability of solid dry salts to conduct electric current explains why the cell has an open-circuit voltage even when the alkali is in the dry solid state. The open-circuit voltage also increases exponentially with rise in temperature.

The process of conduction in the molten state is electrolytic. The type of conduction in the solid state depends on the type of solid and may be electrolytic[13,14,15]; electronic because of lattice imperfections, as in extrinsic semiconductors,[16] or thermally excited electrons, as in intrinsic semiconductors; or both electrolytic and electronic. Regardless of the type of conduction in the solid state, cells made with solid electrolytes of the type given in this paper do have measurable voltages.

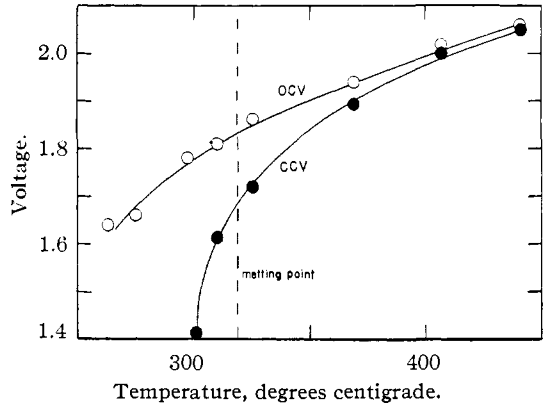

Fig. 4.—Variation of the open- and closed-circuit voltage of the cell Mg: molten NaOH: MnO_2: C with temperature above the melting point of the alkali.

In order to ascertain the effect of temperature on the voltages of the cell in the molten state, the cell was heated considerably above the melting point of the alkali. Data are given in Fig. 4. Both the open- and closed-circuit voltages increase with rise in temperature and approach each other in value; in fact, they differ by only 0.01 v. at 441°. The common primary cells like the Leclanché dry cell show similar differences between open- and closed-circuit voltages with rise in temperature. In other words the internal resistance of the cell becomes less at higher temperatures owing largely to increased mobility and diffusion of the ions.

Czepinski[17] found that the e. m. f. decrease with rise in temperature for cells of the type, silver: molten halide: halogen. As the e. m. f. for this type of cell is equivalent to the decomposition voltage of the halide the e. m. f. should decrease with rise in temperature corresponding to the tendency for the halide to decompose more and more. The reactions in the cells studied in this work are not ones of decomposition or formation and the e. m. f. may, therefore, either increase or decrease with rise in temperature.

The data so far presented indicate that cells with molten electrolytes are very similar in their behavior to the usual types of primary cells. This may be shown more conclusively by discharges of the cells. Cells maintained at 325° were discharged at a low-current drain through a 100-ohm coil. Data obtained with the two-cell designs are given in Fig. 5. The data obtained in the two experiments are in close agreement and the cell shows a fairly flat discharge curve. Data obtained during the initial part of the discharge show differences. This observation is typical of many primary cells and is caused by the conditions of the surface of the magnesium, the distribution of the electrolyte, and other factors that contribute to the "irreversible effects" of the cell.

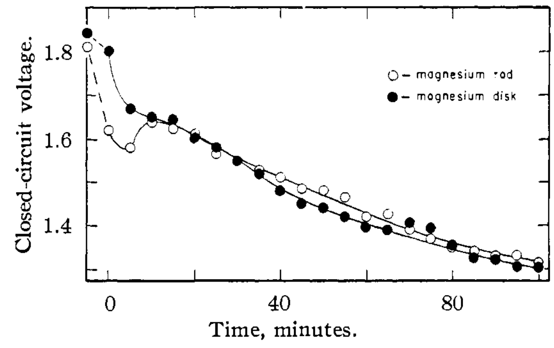

Fig. 5.—Data for the discharge of the cell, Mg: molten NaOH: MnO_2: C.

A longer discharge of the cell of design 2 is shown in Fig. 6. Seven hundred and fifty minutes of service to a terminal voltage of 1.0

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[13] E. Lorenz, "Electrolyse geschmolzener Salze, Monographien und angew. Electroch," 20 (1905); C. Tubandt and E. Lorenz, *Z. physik. Chem.*, **87**, 513 (1914).

[14] C. Tubandt and S. Eggert, *Z. anorg. Chem.*, **110**, 196 (1920).

[15] T. W. Richards and W. N. Stull, *Z. physik. Chem.*, **42**, 621 (1903).

[16] H. C. Torrey and C. A. Whitmer, "Crystal Rectifiers," M. I. T. Radiation Lab. Series, Vol. 15, Chap. 3, 1948.

[17] V. Czepinski, *Z. anorg. Chem.*, **19**, 208 (1899).

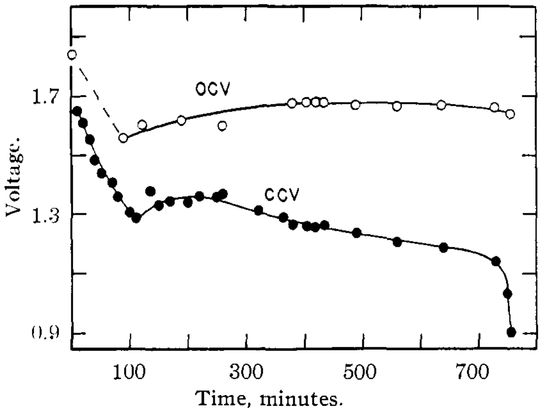

Fig. 6.—Data for a long discharge of the cell Mg: molten NaOH: MnO_2: C, using a magnesium disk.

volt were obtained at an average working voltage of 1.3 volts. Consequently 0.16 ampere-hour of service, corresponding to an efficiency of use of manganese dioxide of 69%, was obtained. This efficiency is only slightly less than that obtained in the Leclanché dry cell on the same light current drain to a cut-off voltage of 1.0 volt. Therefore, in this cell there can be little chemical action, local action, or film or crystal formation of the type frequently found in electrowinning or in electrolysis of fused salts.[18]

Discharges were also made through external resistances of 100, 50, 25 and 10 ohms at 345°. During the first five minutes of the discharge the working voltages were, respectively, 1.62, 1.50, 1.28 and 0.84 volts, corresponding to current densities, respectively, of 0.023, 0.042, 0.072, and 0.12 amp./sq. cm. of electrode surface. These data show the effect of current density on the sustained voltages of the cells and may be used to estimate the size of cells required for desired sustained voltages or current densities at specified working voltages.

The reactions at the anode, cathode, and the over-all cell reaction are, respectively

$$Mg + 2OH^- = Mg(OH)_2 + 2\epsilon$$
$$2MnO_2 + 2Na^+ + 2\epsilon = Mn_2O_3 + Na_2O$$
$$Mg + 2MnO_2 + 2NaOH = Mg(OH)_2 + Mn_2O_3 + Na_2O$$

The formation of $Mg(OH)_2$ and Mn_2O_3 were confirmed by X-ray diffraction patterns. Identification of sodium oxide could not be confirmed, since on removing it from the cell it absorbed water too rapidly for X-ray studies. The magnesium hydroxide covers the magnesium rod loosely and not as an adhering oxide film and as a consequence the anodic reaction continues for an appreciable time. The Mn_2O_3 and sodium oxide form at the cathode and become intimately mixed with unreduced manganese dioxide.

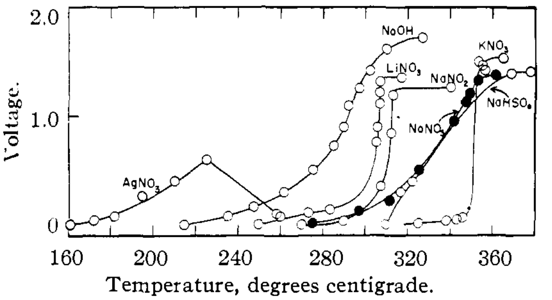

Fig. 7.—Closed-circuit voltages of the cells Mg: molten electrolyte: MnO_2: C, as a function of the temperature in degrees centigrade.

In order to see whether other electrolytes may be used a number of salts were tried. Closed-circuit voltages as a function of temperature are shown in Fig. 7. Silver nitrate is included to show what occurs when short-circuiting occurs within the cell. When silver nitrate becomes molten the silver migrates to the magnesium, covering its surface, whereby short-circuiting occurs. These data may also be presented as evidence that the voltages observed in cells of this type are not contact voltages or a result of thermo-electric effects.

Data obtained when these cells were discharged through a 100-ohm coil are given in Fig. 8.

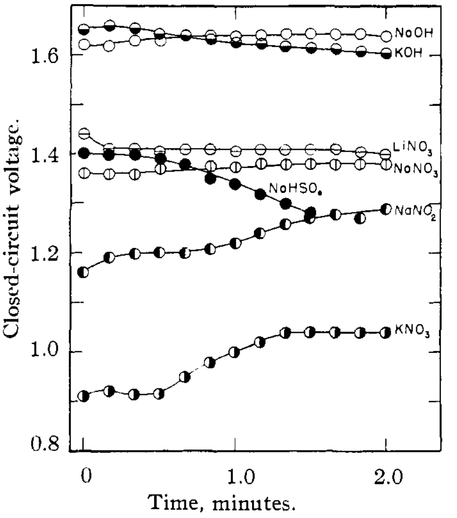

Fig. 8.—Short discharges of the cells Mg: molten electrolyte: MnO_2: C.

It is interesting that the closed-circuit voltages of cells with different electrolytes are in the same order as the conductivity of the electrolytes in the molten state.[19] Sodium and potassium hydroxides gave the highest closed-circuit voltages; they also have the highest conductivity in the molten state. However, longer discharges of the better electrolytes, shown in Fig. 9, indicate that some chemical reaction probably occurs between the magnesium and the salts, since the observed

[18] C. G. Fink and C. C. Ma, *Trans. Electrochem. Soc.*, **84**, 33 (1943); C. G. Fink and D. N. Solanki, *ibid.*, **91**, 203 (1947).

[19] F. M. Jaeger and B. Kapma, *Z. anorg. Chem.*, **113**, 27 (1920); "I. C. T.," McGraw-Hill Book Co., New York, N. Y., 1929, Vol. VI, p. 147-151.

differences are too large to be explained solely by differences in the conductivities of the electrolyte. The cell reactions when the salts are used are the same as those given for sodium hydroxide except that the corresponding magnesium salts are formed.

The same principles should apply to cells constructed with salts of lower melting points than those used in this investigation. Eutectic salt mixtures should serve this purpose. As the voltages were measured when there was a net flow of electric current, thermodynamic data cannot be given. It may be stated, however, that different voltages obtained for different electrolytes must correspond, in part, to the differences in the free energy of formation of the various magnesium salts. The cell reaction is exothermic at high temperatures but insufficient heat is evolved to maintain the cell reaction.

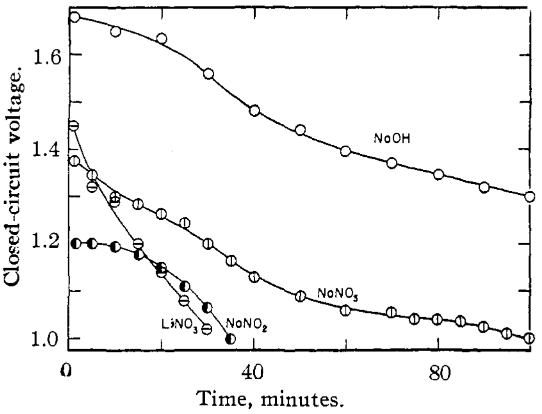

Fig. 9.—Long discharges of the cells Mg: molten electrolyte: MnO$_2$: C.

Summary

Data are presented for the galvanic cell, magnesium: solid or molten electrolyte: manganese dioxide: C over a temperature range extending from room temperature to and above the melting point of the solid. Several electrolytes were studied with sodium hydroxide being the best. The cell has open-circuit voltages which increase as a function of temperature. However, the cell does not sustain a voltage until the melting point of the electrolyte is reached and exceeded. Cells of this type may be activated by heat.

The difference between the open- and closed-circuit voltages of the cell becomes negligible at temperatures considerably above the melting point of the electrolyte.

The cell reaction was postulated for an electrolyte of molten sodium hydroxide and was confirmed in part by X-ray diffraction studies.

WASHINGTON, D. C. RECEIVED JUNE 22, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MERCK & CO., INC.]

The Catalytic Reduction of the Esters of Tartaric Acid to the Erythritols

BY NELSON R. TRENNER AND FREDERICK A. BACHER

A perusal of the literature prior to 1940 concerning the catalytic reduction of the esters of α-hydroxy aliphatic dibasic acids to the corresponding glycols reveals the opinion that in general such reductions cannot be successfully accomplished in the presence of a copper chromite catalyst and at about 250° since marked hydrogenolysis at one or more of the C–O bonds takes place.[1] In view, however, of the possibility, also suggested by Adkins, that the hydrogenolytic reactions take place subsequent to the formation of the glycol and of the further possibility that such hydrogenolytic reactions require a higher activation energy[2] than does the ester reduction, there would follow the possibility that the use of lower temperatures would result in the desired reduction of the ester groups without the occurrence of significant hydrogenolysis. An investigation of the behavior of the dialkyl tartrates in the presence of copper chromite catalyst and in the temperature range of 150 to 200° revealed that these speculations are indeed confirmed and that successful ester reductions to the corresponding tetrahydroxybutanes may be achieved without significant hydrogenolysis.

Experimental

Dialkyl Tartrates.—*meso*-Tartaric acid was prepared from *d*-tartaric acid by means of hot alkali isomerization followed by removal of the *d*- and *l*-isomers as the potassium salts and precipitation of lead *meso*-tartrate.[3] Esterification of the lead salt was effected through the use of alcoholic hydrogen chloride. The crystalline esters were isolated, purified and identified in the usual manner. The dialkyl *meso*-tartrates used in the reductions reported here had the following melting points: dimethyl ester 113–114° (capillary); diethyl ester 56–57° (capillary). The diethyl *d*-tartrate diacetate melted 67–68° (capillary). Diethyl *d*-tartrate is a liquid and it was characterized by means of its ultimate analysis and optical rotation $[\alpha]^{23}\text{D}$ +7.5°.

Anal. Calcd. for $C_8H_{14}O_6$: C, 46.6; H, 6.80. Found: C, 46.7; H, 6.86.

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(1) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," The University of Wisconsin Press, Madison, Wis., 1937, p. 104.

(2) In referring to the activation energy concept we here assume that this quantity *essentially* determines the relative reaction rates involved and that other factors such as relative degrees of adsorption on the catalyst surface, the nature of the rate determining steps, etc., are substantially constant for the various reactants involved in this investigation. This would seem reasonably justified provided we confine our speculations to molecules of the same general type and size and to a relatively small temperature range.

(3) Beilstein III, fourth edition, 1921, p. 529.