THERMODYNAMIC FRAMEWORK FOR ESTIMATING THE OVERALL THERMAL, COULOMBIC, AND VOLTAGE EFFICIENCIES OF ALKALINE BATTERIES AS A FUNCTION OF CONCENTRATION AND TEMPERATURE

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The aim of this research is to define the thermodynamic properties of Fe, Ni, Zn, Al and Li in concentrated LiOH, NaOH, and KOH solutions as a function of temperature (-20 °C to 120 °C) and concentration (1 to 12 mol kg^{-1}). These data are required to assess quantitatively the efficiencies of various alkaline batteries.

Quantitative assessment of the efficiencies of various alkaline battery systems requires detailed knowledge of the thermodynamic properties of the electrode materials in concentrated hydroxide solutions over a wide range of concentration and temperature. Consideration of the nonideal behavior of concentrated hydroxide solutions is essential for determining the thermodynamic stability and electrochemical performance of battery electrodes and for selecting the optimum conditions under which various battery systems should operate.

Vapor pressure determination

Insufficient data are available for concentrated LiOH solutions, particularly with regard to vapor pressures from which water activities, osmotic coefficients, and stoichiometric mean activity coefficients can be calculated. Therefore, vapor pressures of concentrated LiOH/H$_2$O solutions have been determined experimentally as a function of concentration (0.5 to 5 molal) and temperature (-10 °C to 120 °C). Two different experiments were performed to obtain vapor pressure data over the desired temperature range. In one set of experiments, vapor pressure data were measured directly from 0 to 60 °C. To expand the temperature range (-10 to 120 °C), a second set of data were obtained by measuring the boiling points of lithium hydroxide solutions as a function of concentration.

Thermodynamic functions for concentrated hydroxide solutions

Data for the activity of water, stoichiometric mean activity coefficient, and the mean ionic activity coefficient for the solute in concentrated KOH, NaOH, and LiOH were obtained as a function of concentration and temperature. The activity of water is seen to decrease substantially with increasing

stoichiometric concentration, with the effect being most pronounced at the lowest temperature. The activity coefficients also vary substantially with concentration and temperature. Significant differences are observed between the stoichiometric and mean ionic activity coefficients for the LiOH and NaOH systems, but not for KOH solutions. This difference is due to the greater extent of ion pairing in concentrated LiOH and NaOH solutions than in KOH solutions.

Calculation of pH of concentrated hydroxide solutions

The pH of concentrated hydroxide solutions was calculated and plotted as a function of concentration and temperature. It is observed that the pH for all these media passes through a maximum as the concentration of the solute is increased through the range 2 to 6 mol kg^{-1}. The maximum in pH results from the competing effects of ion pairing, the variation in the activity of water, and the variation in the mean activity coefficient with concentration. It is also observed that the pH decreases along the series LiOH– < NaOH–KOH for any given stoichiometric concentration. This is expected, because the ion pairing increases in the order LiOH > NaOH > KOH.

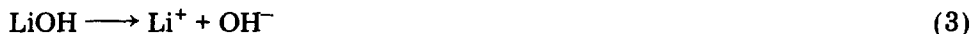## Thermodynamic functions for metal/hydroxide systems

A computer program has been prepared to calculate the potential–pH relations for various equilibrium phenomena for the metals Ni, Fe, Zn, Al, and Li in concentrated LiOH, NaOH, and KOH solutions over the temperature range --20 to 120 °C. The program contains facilities for computing the activity of water and the pH of the medium for any given system, and hence for calculating the equilibrium potentials for each reaction at various stoichiometric concentrations of alkali hydroxide. The program is also capable of handling mixed metal oxidation products, such as $NiFe_2O_4$, which may form because of transport of the soluble products from one electrode to the other in an actual battery system.

The various possible reactions being considered in describing the equilibrium properties of Ni, Fe, Zn, Al, and Li in concentrated hydroxide solutions have been formulated. The necessary thermodynamic parameters have been selected from the literature or have been estimated, where necessary.

As an example of the kind of data this study has produced, the Li/LiOH system is considered briefly below. In lithium–water batteries, a semipassivated lithium anode is employed. A lithium-metal anode and an iron-wire mesh are brought into direct contact with an aqueous electrolyte. Water serves as the active cathode material in this cell. Lithium, despite being the most reducing of the alkali metals, is relatively more stable in the presence of water than is sodium or potassium. This is the consequence of an adherent surface film that develops under certain conditions   of polarization and

electrolyte composition. This film prevents the catastrophic corrosion of the metal.

Stability diagrams were computed for the following half-cell reactions.

$$LiOH + e^- \longrightarrow Li + OH^- \tag{1}$$

$$Li^+ + e^- \longrightarrow Li \tag{2}$$

$$LiOH \longrightarrow Li^+ + OH^- \tag{3}$$

It has been observed in previous studies, and for these reactions also, that the thermodynamic equilibrium relationships for metals in concentrated hydroxide media are expressed better in the form of E *versus* log m_{MOH}, than as the more traditional E *versus* pH equations. The cell potential was plotted for reaction (1) as a function of LiOH concentration and temperature. These plots delineate the region within which different species (Li, LiOH) are stable, i.e., below the line the reduced species (Li) is stable, whereas above the line the oxidized species (LiOH) is stable. It was found that the stability region for the oxidized species increases with an increase in temperature, while that of reduced species is reduced.

The research will be completed by the end of 1982.

Recent publications

1 B. K. Sundararaj, Thermodynamics of lithium/lithium hydroxide/water system, M.S. Thesis, The Ohio State University, 1982.
2 B. K. Sundararaj, R. P. Singh and D. D. MacDonald, The thermodynamics of alkaline battery system, *Proc. 16th Intsoc. Energy Conversion Eng. Conf.*, Am. Soc. Mech. Eng., 1981.

AN ELECTROCHEMICAL AND MORPHOLOGICAL STUDY OF THE EFFECT OF TEMPERATURE ON THE RESTRUCTURING AND LOSS OF CAPACITY OF ALKALINE BATTERY ELECTRODES

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The objectives of this research program are to investigate the effect of temperature on the restructuring of porous alkaline battery electrodes and to determine the mechanisms of degradation of charge capacities of the electrodes on repetitive cycling. The original objectives included study of porous iron, nickel, and zinc electrodes. However, later redefinition of the program goals restricted the work to porous nickel electrodes in concentrated potassium hydroxide solutions.