

A THERMODYNAMIC FRAMEWORK FOR ESTIMATING THE EFFICIENCIES OF ALKALINE BATTERIES

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Summary

A thermodynamic framework has been developed to evaluate the efficiencies of alkaline battery systems for electrolyte (MOH) concentrations from 1 to 8 mol kg⁻¹ and over the temperature range -10 to 120 °C. An analysis of the thermodynamic properties of concentrated LiOH, NaOH, and KOH solutions was carried out to provide data for the activity of water, the activity coefficient of the hydroxide ion, and the pH of the electrolyte. Potential-pH relations were then derived for various equilibrium phenomena for the metals Li, Al, Fe, Ni, and Zn in aqueous solutions and, using the data for the alkali metal hydroxides, equilibrium potentials were computed as a function of composition and temperature. These data were then used to calculate reversible cell voltages for a number of battery systems, assuming a knowledge of the cell reactions. Finally, some of the calculated cell voltages were compared with observed cell voltages to compute voltage efficiencies for various alkaline batteries.

The voltage efficiencies of H₂/Ni, Fe/Ni, and Zn/Ni test cells were found to be between 90 and 100%, implying that, at least at open circuit, there is little, if any, contribution from parasitic redox couples to the cell potentials for these systems. The efficiency of an Fe/air test cell was relatively low (72%). This is probably due to the less-than-theoretical voltage of the air electrode.

Introduction

High energy alkaline batteries are under consideration for vehicular propulsion and standby power source applications. Leading candidate battery systems for these applications include zinc-nickel, iron-nickel,

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hydrogen-nickel, zinc-air, iron-air, lithium-air, and aluminum-air. Some of these systems, *e.g.*, iron-nickel and H_2/Ni , have already undergone substantial development, whereas others, *e.g.*, aluminum-air, are in a research stage. The rational choice of the most suitable battery will involve a compromise between various characteristics that define the performance of the system; cost, energy, power, and conversion efficiency on both charging and discharging. This latter parameter is particularly important in the case of vehicular propulsion because the battery (with the exception of mechanically recharged systems, *e.g.*, Al-air) will be subjected to extensive deep cycling, and will have to compete with the more traditional fossil-fueled systems.

A complete analysis of the efficiency of an electrochemical energy storage or conversion system requires a knowledge of the thermodynamic properties of the cell components. Thus, the overall and thermal efficiencies of the device may be defined, respectively, as:

$$\epsilon = - \left[\int_{\alpha=0}^{\alpha=q} E_c d\alpha \right] / \Delta G \quad (1)$$

$$\epsilon_T = - \left[\int_{\alpha=0}^{\alpha=q} E_c d\alpha \right] / \Delta H \quad (2)$$

where ΔG is the molar free energy change, ΔH is the molar enthalpy change, α is the charge transferred through the external circuit, and E_c is the cell voltage. The symbol q is the total charge passed through the external circuit per mole of cell reaction; q may be less than, or equal to, nF where n is the stoichiometric number of electrons involved in the cell reaction, and F is the Faraday. A value for q of less than nF can arise from internal "chemical shorting" due to diffusion of anodic dissolution products (*e.g.*, $Zn(OH)_4^{2-}$, FeO_2^{2-}) to the cathode and from transport of cathodic products to the anode.

The voltage efficiency of the cell and the coulombic efficiency of a half-cell reaction are defined as:

$$\epsilon_v = E_c/E_R \quad (3)$$

and

$$\epsilon_c = q/nF \quad (4)$$

respectively, where E_R is the reversible potential for the cell.

Evaluation of the efficiency of any given battery requires the experimental determination of q and E_c during both charging and discharging, a knowledge of the reactions taking place in the system to determine n , and an analysis of the thermodynamics of the cell to yield ΔG , ΔH , and E_R . It should be noted that E_R is often equated to the open-circuit potential, but this is valid only in the absence of any internal shorting phenomena

or parasitic reactions which may cause a deviation of the half-cell potentials from their equilibrium values.

The evaluation of the thermodynamic quantities ΔG and ΔH involves not only a consideration of the reactions and products in their standard states, but also a knowledge of the activity coefficients of dissolved ions and activity of the solvent in the concentrated electrolyte solutions of interest. The efficiency of an electrochemical energy storage system is expected to vary with temperature, and it is therefore desirable to evaluate the thermodynamic parameters over a wide range of environmental conditions.

Extensive thermodynamic data of the type required are available for *dilute* systems over a wide range of temperatures. Few data have been generated, however, for the metals of interest (Fe, Ni, Zn, Al, and Li) in concentrated alkali solution ($> 1 \text{ mol kg}^{-1}$) and over the temperature range (-10 to 120°C) which is expected for some applications. In this paper a study which has been carried out to assess the thermodynamic properties of the metals of interest in concentrated LiOH, NaOH, and KOH media as a function of composition and temperature is described. The thermodynamic data generated have been used to compute equilibrium potentials for a large number of reactions involving Fe, Ni, Zn, Al and Li in the concentrated LiOH, NaOH and KOH solutions ($1 - 8 \text{ mol kg}^{-1}$) at temperatures from -10 to 120°C . These data are subsequently used to calculate reversible cell potentials for a number of battery systems, assuming a knowledge of the cell reactions. The calculated cell voltages are then compared with observed cell voltages to compute voltage efficiencies for various alkaline batteries.

Thermodynamics of concentrated alkali hydroxide solutions

Concentrated solutions of alkali metal hydroxides exhibit non-ideal behaviour. The activity of the solvent, in this case water, cannot be assumed to be unity, and depends upon the identity of the cation (Li^+ , Na^+ , K^+), contrary to the behaviour in dilute solutions. Furthermore, the activity of the alkali metal hydroxide varies with concentration and temperature in a non-ideal manner as short range interactions become significant when the mean distance between the solute particles is small [1, 2]. The activity coefficient of the hydroxide ion in solution is also affected by the cation because of ion pair formation which increases along the series $\text{KOH} < \text{NaOH} < \text{LiOH}$ [3 - 6].

If the vapour pressure is low enough that fugacity corrections can be ignored, the activity of water in solution can be found from Raoult's law as

$$a_w = p/p^\circ \quad (5)$$

where p and p° are the vapour pressures of the solution and pure water, respectively. The pressures are low enough up to 120°C for the error incurred by ignoring fugacity coefficient corrections to be estimated [7] as no more than a few percent.

The osmotic coefficient for the medium, ϕ , is related to the activity of water by eqn. (6)

$$\phi = -1000 \ln a_w / M\nu m \quad (6)$$

where M is the molecular weight of H_2O , m is the molality of the electrolyte and ν is the number of ions into which the electrolyte dissociates in solution ($\nu = 2$ for the alkali metal hydroxides). According to the Gibbs–Duhem equation, the change in the mean molal activity coefficient of the solute with concentration is given by

$$d \ln \gamma_{\pm} = -(1/m) d[m(1 - \phi)] \quad (7)$$

which, on integration over the limits of concentration of 0 to m , yields

$$\ln \gamma_{\pm} = -(1 - \phi)2 \int_0^m \left(\frac{1 - \phi}{m} \right) d m^{1/2} \quad (8)$$

Evaluation of the integral in eqn. (8) therefore allows the activity coefficient γ_{\pm} to be determined.

The observed uncertainty in the osmotic coefficient at low concentrations increases sharply as m is decreased. Consequently, the variation of $(1 - \phi)$ with $m^{1/2}$ is more satisfactorily described by using Debye–Hückel theory [6] which predicts that for low concentrations

$$(1 - \phi)/m^{1/2} = 0.7676 A d_0^{1/2} \sigma_m \quad (9)$$

where d_0 is the density of the solvent and

$$\sigma_m = \sum_{n=1}^{\infty} \left(\frac{3n}{n+2} \right) (-A_m' m^{1/2})^{n-1} \quad (10)$$

The Debye–Hückel coefficients are given by

$$A = 1.814 \times 10^6 / (DT)^{3/2} \quad (11)$$

$$A_m' = 153 / (DT)^{1/2} \quad (12)$$

where D is the dielectric constant of water at the temperature of interest (T K). The data of Akerlof and Oshry [8] for D as a function of temperature were used for the evaluation of A and A_m' .

Previous work [7] has shown that the upper concentration limit for eqn. (9) is 0.8 mol kg^{-1} . Hence, $(1 - \phi)/m^{1/2}$ can be calculated over the low concentration range ($0 - 0.8 \text{ mol kg}^{-1}$) using eqn. (9), but for higher concentrations this function must be evaluated from experiment using eqn. (6).

In this study, $\ln \gamma_{\pm}$ was calculated from eqn. (8) by an iterative technique using the trapezoidal rule to evaluate the integral. The $m^{1/2}$ field was divided into 80, 160, 320, 640, 800, and 1600 increments to determine the minimum number required to achieve an acceptable level of precision.

The effect of varying the number of integration increments on the values of $\log \gamma_{\pm}$ calculated using eqn. (8) for NaOH is shown in Table 1. In all cases, $\log \gamma_{\pm}$ becomes more positive as the increments are made smaller. There is little change in $\log \gamma_{\pm}$ as N is increased from 320 to 1600 increments, however, and, therefore, the values given by $N = 1600$ are regarded as sufficiently precise for subsequent pH calculations.

The definition of pH as $-\log a_{\text{H}^+}$ was retained for the concentrated hydroxide systems treated in this study on the basis that it is a purely formal relationship requiring a_{H^+} itself to be specified. In the absence of more reliable data for quantities such as γ_{\pm} , this definition is considered to provide an adequate estimate of the pH. Accordingly, the pH of concentrated hydroxide solutions could be calculated using either the ionic product of water, Q_w , or the dissociation constant, K_w , of water. Values of Q_w reported in the literature [9], however, were derived from experimental studies with KCl solutions and, furthermore, are valid only for concentrations less than 3.0 mol kg^{-1} . It would therefore be necessary to assume that the same values of Q_w hold for concentrated hydroxide solutions.

In order to avoid this assumption, it was decided to use in this analysis the dissociation constant which is given by

$$K_w = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_w} \quad (13)$$

An expression for K_w as a function of temperature is given by Naumov *et al.* [10]. Introduction of K_w and rearrangement leads to the following equation for the pH

$$\text{pH} = \log \frac{m_{\text{OH}^-} \gamma_{\pm}^*}{a_w} + \frac{4466.2}{T} - 5.941 + 0.016 638T \quad (14)$$

where γ_{\pm}^* is the mean ionic activity coefficient and m_{OH^-} is the concentration of free hydroxide ions. In concentrated solutions, m_{OH^-} differs from

TABLE 1

The effect of the number of integration increments on the values of $\log \gamma_{\pm}$ for NaOH

| T (K) | m (mol kg^{-1}) | Log γ_{\pm} | | | | | |
|------------|-----------------------------------|------------------------------|--------|--------|--------|--------|--------|
| | | Number of increments (N) | | | | | |
| | | 80 | 160 | 320 | 640 | 800 | 1600 |
| 298 | 1 | -0.171 | -0.167 | -0.165 | -0.164 | -0.164 | -0.164 |
| | 4 | -0.104 | -0.100 | -0.098 | -0.097 | -0.097 | -0.096 |
| | 8 | 0.225 | 0.229 | 0.231 | 0.232 | 0.232 | 0.233 |
| 393 | 1 | -0.266 | -0.263 | -0.261 | -0.261 | -0.261 | -0.260 |
| | 4 | -0.256 | -0.253 | -0.252 | -0.251 | -0.251 | -0.251 |
| | 8 | -0.129 | -0.126 | -0.125 | -0.124 | -0.124 | -0.124 |

the stoichiometric concentration, m_{MOH} , of alkali metal hydroxide due to ion pairing:

$$m_{\text{MOH}} = m_{\text{OH}^-} + m_{\text{comp}} \quad (15)$$

where m_{comp} is the concentration of ion pairs. Similarly, γ_{\pm}^* refers to the actual dissociated species whereas γ_{\pm} is based on the stoichiometric concentration scale. For those solutes which form simple 1:1 ion pairs, the product ($m_{\text{OH}^-}\gamma_{\pm}^*$) may be evaluated using the following relationship [11]:

$$m_{\text{OH}^-}\gamma_{\pm}^* = m_{\text{MOH}}\gamma_{\pm} \quad (16)$$

The pH equation can now be expressed as

$$\text{pH} = \frac{m_{\text{MOH}}\gamma_{\pm}}{a_w} + \frac{4466.2}{T} - 5.941 + 0.016638T \quad (17)$$

Clearly, in order to evaluate the pH, as well as γ_{\pm} from eqn. (8), the activity of water must be known at the appropriate concentration of each hydroxide solution. Sufficient data are available in the literature for the vapour pressures of NaOH and KOH solutions over the desired concentration and temperature ranges, thereby allowing values of a_w to be obtained using eqn. (5). Vapour pressure data for KOH were taken from the work of Anisimov [12], and from that of Bro and Kang [13], while those for NaOH were calculated using the following equation derived by MacMullin [14]:

$$\frac{p}{p^{\circ}} = 1 + [(T - 174)(a + bm + cm^2 + d/m) - 0.03170]m \quad (18)$$

where m is the molality of the solution, p° is the vapour pressure of pure water at temperature T ($^{\circ}\text{C}$), and the coefficients a , b , c , and d have the following values:

$$a = -8.6715 \times 10^{-5}$$

$$b = 3.368 \times 10^{-5}$$

$$c = -1.354 \times 10^{-6}$$

$$d = 7.88 \times 10^{-5}$$

Equation (18) is only valid for temperatures between 20 and 100 $^{\circ}\text{C}$, but it is assumed that extrapolation to -10° and to 120 $^{\circ}\text{C}$ can be made with negligible error. Equation (18) is also valid for $m < 12.5 \text{ mol kg}^{-1}$, which therefore included the solutions of interest in this work.

The vapour pressure data for both NaOH and KOH solutions were plotted against concentration for each temperature, and a smoothed set of data over the desired concentration range was selected. A statistical analysis of the smoothed data was performed to obtain the most appropriate polynomials to describe the variation of the activity of water with concentration at each temperature. Accordingly, values were determined for the coefficient in eqn. (19),

$$\frac{p}{p^{\circ}} = \sum_{i=0}^k A(i)m^i \quad (19)$$

and these are listed in Tables 3 and 4.

Insufficient vapour pressure data were available for LiOH to generate values of a_w . As a result, these data had to be obtained from an experimental

TABLE 2

Polynomial coefficients for best fit of p/p° vs. concentration for lithium hydroxide

| T (°C) | p/p° | | | |
|-------------|---------------|-----------|-----------|-----------|
| | A(0) | A(1) | A(2) | A(3) |
| -10 | 0.992 64 | -0.030 85 | 0.0 | 0.0 |
| 0 | 1.000 59 | -0.031 77 | 0.0 | 0.0 |
| 10 | 0.997 59 | -0.026 36 | -0.000 96 | 0.0 |
| 20 | 0.999 69 | -0.029 83 | -0.000 05 | 0.0 |
| 25 | 1.000 95 | -0.030 91 | 0.0 | 0.0 |
| 30 | 0.998 88 | -0.028 92 | 0.0 | -0.000 06 |
| 40 | 1.000 48 | -0.030 12 | 0.0 | 0.0 |
| 50 | 0.999 80 | -0.029 71 | 0.0 | 0.0 |
| 60 | 0.999 75 | -0.029 09 | 0.0 | 0.0 |
| 70 | 1.000 04 | -0.028 81 | 0.0 | 0.0 |
| 80 | 0.999 96 | -0.028 45 | 0.0 | 0.0 |
| 90 | 1.003 17 | -0.035 24 | 0.004 81 | -0.001 01 |
| 100 | 1.001 37 | -0.029 05 | 0.0 | 0.0 |
| 110 | 1.001 95 | -0.030 62 | 0.000 70 | 0.0 |
| 120 | 1.001 79 | -0.029 88 | 0.000 50 | 0.0 |

TABLE 3

Polynomial coefficients for best fit of p/p° vs. concentration for sodium hydroxide

| T (°C) | p/p° | | | |
|-------------|---------------|-----------|-----------|----------|
| | A(0) | A(1) | A(2) | A(3) |
| -10 | 0.984 44 | -0.015 66 | -0.006 19 | 0.000 25 |
| 0 | 0.988 37 | -0.018 03 | -0.005 65 | 0.000 23 |
| 10 | 0.989 04 | -0.018 81 | -0.005 33 | 0.000 21 |
| 20 | 0.989 71 | -0.019 59 | -0.005 00 | 0.000 20 |
| 25 | 0.986 11 | -0.017 60 | -0.005 20 | 0.000 21 |
| 30 | 0.992 19 | -0.024 87 | -0.002 97 | 0.000 01 |
| 40 | 0.991 04 | -0.021 17 | -0.004 35 | 0.000 17 |
| 50 | 0.991 63 | -0.021 90 | -0.004 03 | 0.000 16 |
| 60 | 0.992 18 | -0.022 03 | -0.003 98 | 0.000 16 |
| 70 | 0.993 05 | -0.023 53 | 0.003 38 | 0.000 14 |
| 80 | 0.993 71 | -0.024 31 | -0.003 05 | 0.000 12 |
| 90 | 0.994 38 | -0.025 10 | -0.002 73 | 0.000 11 |
| 100 | 0.995 05 | -0.025 89 | -0.002 40 | 0.000 09 |
| 110 | 0.995 72 | -0.026 66 | -0.002 08 | 0.000 08 |
| 120 | 0.996 39 | -0.027 46 | -0.001 75 | 0.000 07 |

TABLE 4

Polynomial coefficients for best fit of p/p° vs. concentration for potassium hydroxide

| T (°C) | p/p° | | | |
|-------------|-------------|-----------|------|------|
| | A(0) | A(1) | A(2) | A(3) |
| -10 | 0.982 15 | -0.058 55 | 0.0 | 0.0 |
| 0 | 1.026 269 | -0.057 75 | 0.0 | 0.0 |
| 20 | 1.011 06 | -0.055 47 | 0.0 | 0.0 |
| 25 | 1.018 776 | -0.058 03 | 0.0 | 0.0 |
| 40 | 1.016 83 | -0.054 51 | 0.0 | 0.0 |
| 60 | 1.019 61 | -0.054 04 | 0.0 | 0.0 |
| 80 | 1.017 00 | -0.052 48 | 0.0 | 0.0 |
| 100 | 1.015 04 | -0.050 95 | 0.0 | 0.0 |
| 120 | 1.011 96 | -0.049 24 | 0.0 | 0.0 |

study which is described elsewhere [15]. As with NaOH and KOH, the LiOH data were subjected to a statistical analysis and the resulting values for the polynomial coefficients are given in Table 2.

Properties of concentrated alkali hydroxide solutions

Values of a_w , $\log \gamma_{\pm}$ and pH for concentrated LiOH, NaOH, and KOH solutions are given in Tables 5, 6, and 7, respectively, as a function of temperature and concentration. The activity of water is shown in Fig. 1 to decrease markedly as the stoichiometric concentration increases, with the effect being most pronounced at the lowest temperature. By contrast, the value of a_w generally increases with temperature, although in the case of KOH solutions, a_w initially passes through a maximum at 273 K (see Table 5).

$\log \gamma_{\pm}$ is plotted against $m^{1/2}$, as shown in Fig. 2, in order to provide a comparison with previous studies. The data for LiOH at 298 K are in excellent agreement with those quoted by Harned and Owen [6]. In the case of NaOH, there is still reasonable agreement between the calculated and literature [6, 16] data at 298 K, whereas the corresponding data for KOH exhibit a significant difference at concentrations above 1 mol kg⁻¹. In view of the better agreement for LiOH and NaOH for which non-ideal behaviour is expected to be more pronounced, the analysis to obtain $\log \gamma_{\pm}$ appears to be adequate. In the case of KOH, however, it is possible that considerable error may exist in the water activity data used in the calculations, as suggested by the surprisingly linear dependence of a_w on concentration up to 8 mol kg⁻¹.

In general, $\log \gamma_{\pm}$ decreases with increasing temperature, but NaOH ($m \leq 2$ mol kg⁻¹) and KOH solutions initially exhibit a minimum (in this case at 273 K). The dependence of $\log \gamma_{\pm}$ on concentration varies with the

TABLE 5

Activity of water for alkali hydroxide solutions as a function of concentration and temperature

| m (mol kg^{-1}) | a_w | | | | | | | |
|-----------------------------------|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | Temperature (K) | | | | | | | |
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 0.962 | 0.969 | 0.970 | 0.970 | 0.971 | 0.972 | 0.972 | 0.972 |
| 2 | 0.931 | 0.937 | 0.939 | 0.940 | 0.942 | 0.943 | 0.943 | 0.944 |
| 3 | 0.900 | 0.905 | 0.908 | 0.910 | 0.912 | 0.915 | 0.914 | 0.917 |
| 4 | 0.869 | 0.874 | 0.877 | 0.880 | 0.883 | 0.886 | 0.885 | 0.890 |
| 5 | 0.838 | 0.842 | 0.846 | 0.850 | 0.854 | 0.858 | 0.856 | 0.865 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 0.963 | 0.965 | 0.964 | 0.966 | 0.966 | 0.966 | 0.967 | 0.967 |
| 2 | 0.930 | 0.932 | 0.932 | 0.933 | 0.933 | 0.934 | 0.934 | 0.935 |
| 3 | 0.888 | 0.890 | 0.892 | 0.893 | 0.895 | 0.897 | 0.898 | 0.900 |
| 4 | 0.839 | 0.841 | 0.846 | 0.848 | 0.851 | 0.855 | 0.859 | 0.863 |
| 5 | 0.783 | 0.786 | 0.794 | 0.798 | 0.803 | 0.811 | 0.817 | 0.824 |
| 6 | 0.721 | 0.726 | 0.739 | 0.744 | 0.751 | 0.764 | 0.773 | 0.784 |
| 7 | 0.657 | 0.664 | 0.680 | 0.688 | 0.698 | 0.715 | 0.727 | 0.742 |
| 8 | 0.590 | 0.600 | 0.620 | 0.630 | 0.643 | 0.665 | 0.680 | 0.701 |
| <i>KOH</i> | | | | | | | | |
| 1 | 0.924 | 0.969 | 0.961 | 0.962 | 0.966 | 0.965 | 0.964 | 0.963 |
| 2 | 0.865 | 0.911 | 0.903 | 0.908 | 0.912 | 0.912 | 0.913 | 0.913 |
| 3 | 0.807 | 0.853 | 0.845 | 0.853 | 0.857 | 0.860 | 0.862 | 0.864 |
| 4 | 0.748 | 0.795 | 0.787 | 0.799 | 0.803 | 0.807 | 0.811 | 0.815 |
| 5 | 0.689 | 0.738 | 0.729 | 0.744 | 0.749 | 0.755 | 0.760 | 0.766 |
| 6 | 0.631 | 0.680 | 0.671 | 0.690 | 0.695 | 0.702 | 0.709 | 0.717 |
| 7 | 0.572 | 0.622 | 0.613 | 0.635 | 0.641 | 0.650 | 0.658 | 0.667 |
| 8 | 0.514 | 0.564 | 0.555 | 0.581 | 0.587 | 0.597 | 0.607 | 0.618 |

cation; LiOH solutions display a decrease with increasing concentration over the range shown, whereas NaOH exhibits a minimum followed by a marked increase in $\log \gamma_{\pm}$. Similarly, the data for KOH increase subsequent to an apparent minimum, as observed in earlier work [17].

The pH of concentrated hydroxide solutions is shown in Fig. 3 to vary non-linearly with composition, but it nevertheless exhibits a steady increase over the range of molalities shown. It is apparent that the change in pH decreases along the series KOH > NaOH > LiOH for any given stoichiometric concentration. This decrease reflects a corresponding increase in ion pairing for the alkali hydroxides in solution.

Thermodynamics of metals in concentrated alkali solutions

The thermodynamic properties of metals in aqueous media can be derived for reactions having the general form

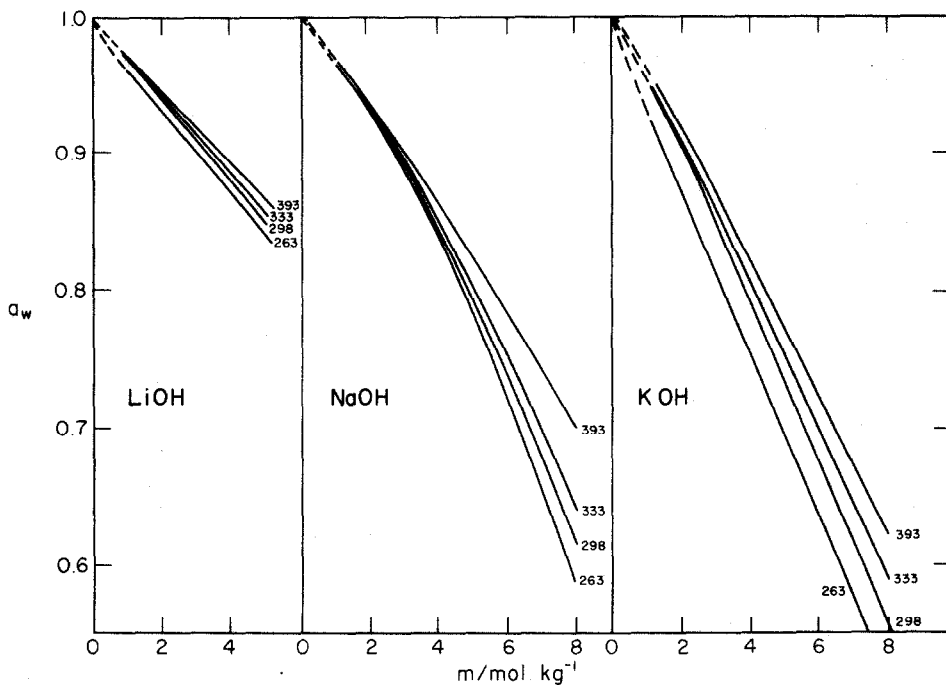


Fig. 1. Variation of the activity of water with concentration of LiOH, NaOH, and KOH solutions as a function of temperature.

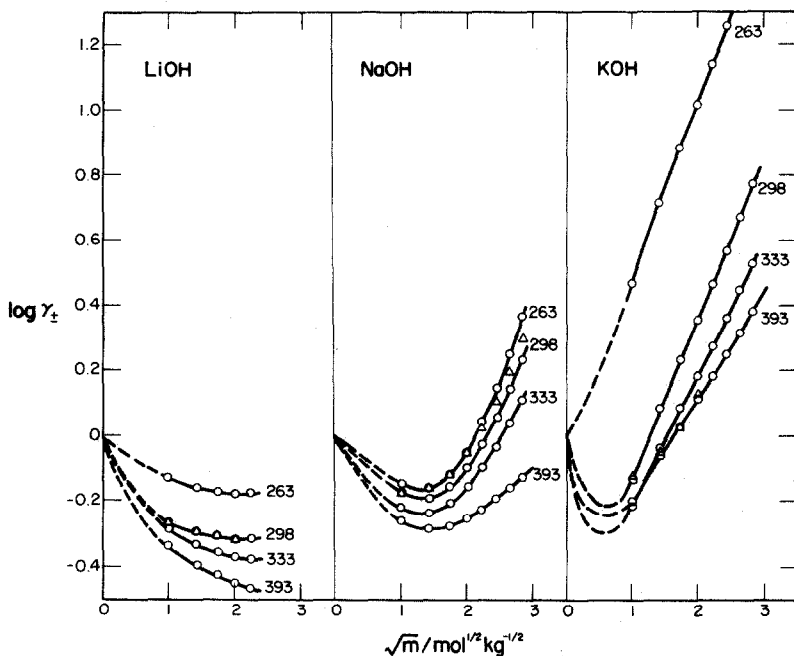


Fig. 2. Variation of the mean molal activity coefficient with concentration in concentrated solutions of LiOH, NaOH, and KOH as a function of temperature. The symbol, Δ , represents literature data [6, 16] at 298 K.

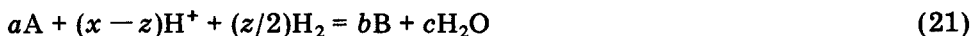
TABLE 6

Mean molal activity coefficients for alkali hydroxide solutions as a function of concentration and temperature

| <i>m</i> (mol kg ⁻¹) | log γ_{\pm} | | | | | | | |
|--|--------------------|--------|--------|--------|--------|--------|--------|--------|
| | Temperature (K) | | | | | | | |
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | -0.129 | -0.241 | -0.266 | -0.275 | -0.287 | -0.307 | -0.329 | -0.340 |
| 2 | -0.158 | -0.264 | -0.297 | -0.314 | -0.334 | -0.361 | -0.377 | -0.393 |
| 3 | -0.170 | -0.272 | -0.310 | -0.331 | -0.357 | -0.387 | -0.400 | -0.426 |
| 4 | -0.174 | -0.273 | -0.315 | -0.339 | -0.370 | -0.403 | -0.413 | -0.449 |
| 5 | -0.174 | -0.270 | -0.315 | -0.342 | -0.376 | -0.412 | -0.421 | -0.468 |
| <i>NaOH</i> | | | | | | | | |
| 1 | -0.144 | -0.179 | -0.164 | -0.203 | -0.220 | -0.230 | -0.244 | -0.260 |
| 2 | -0.164 | -0.191 | -0.190 | -0.217 | -0.235 | -0.247 | -0.263 | -0.280 |
| 3 | -0.117 | -0.144 | -0.155 | -0.182 | -0.205 | -0.225 | -0.247 | -0.271 |
| 4 | -0.043 | -0.073 | -0.096 | -0.127 | -0.156 | -0.187 | -0.217 | -0.251 |
| 5 | 0.046 | 0.011 | -0.025 | -0.061 | -0.097 | -0.141 | -0.179 | -0.224 |
| 6 | 0.145 | 0.103 | 0.056 | 0.012 | -0.031 | -0.089 | -0.136 | -0.193 |
| 7 | 0.252 | 0.203 | 0.142 | 0.091 | 0.039 | -0.034 | -0.090 | -0.159 |
| 8 | 0.365 | 0.307 | 0.233 | 0.173 | 0.112 | 0.024 | -0.042 | -0.124 |
| <i>KOH</i> | | | | | | | | |
| 1 | 0.470 | -0.245 | -0.130 | -0.159 | -0.216 | -0.207 | -0.208 | -0.196 |
| 2 | 0.714 | -0.034 | 0.087 | 0.026 | -0.037 | -0.042 | -0.057 | -0.060 |
| 3 | 0.879 | 0.109 | 0.235 | 0.152 | 0.085 | 0.071 | 0.047 | 0.034 |
| 4 | 1.015 | 0.227 | 0.356 | 0.255 | 0.185 | 0.164 | 0.133 | 0.113 |
| 5 | 1.137 | 0.333 | 0.465 | 0.348 | 0.275 | 0.248 | 0.210 | 0.183 |
| 6 | 1.253 | 0.433 | 0.568 | 0.436 | 0.360 | 0.327 | 0.283 | 0.250 |
| 7 | 1.367 | 0.530 | 0.669 | 0.522 | 0.444 | 0.404 | 0.355 | 0.315 |
| 8 | 1.482 | 0.629 | 0.771 | 0.608 | 0.527 | 0.482 | 0.426 | 0.380 |



where a , x , b and c are stoichiometric coefficients. If the equilibrium potential of reaction (20) is referred to the standard hydrogen electrode at the same temperature [SHE(T)], the cell reaction is



The equilibrium relationship for such a reaction is expressed as

$$E = E^\circ - \frac{2.303RT}{zF} \log \frac{[a_B^b a_{H_2O}^c]}{[a_A^a a_{H^+}^x]} \quad (22)$$

where

$$E^\circ = -\Delta_R G_T^\circ / zF \quad (23)$$

TABLE 7

pH for alkali hydroxide solutions as a function of concentration and temperature

| <i>m</i> (mol kg ⁻¹) | pH | | | | | | | |
|--|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | Temperature (K) | | | | | | | |
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 15.30 | 14.73 | 13.75 | 13.27 | 12.74 | 12.29 | 11.93 | 11.64 |
| 2 | 15.59 | 15.02 | 14.03 | 13.55 | 13.01 | 12.55 | 12.19 | 11.90 |
| 3 | 15.77 | 15.21 | 14.21 | 13.72 | 13.17 | 12.72 | 12.36 | 12.06 |
| 4 | 15.90 | 15.35 | 14.35 | 13.85 | 13.30 | 12.84 | 12.49 | 12.17 |
| 5 | 16.02 | 15.46 | 14.46 | 13.96 | 13.40 | 12.94 | 12.59 | 12.26 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 15.29 | 14.80 | 13.86 | 13.35 | 12.81 | 12.37 | 12.01 | 11.72 |
| 2 | 15.58 | 15.10 | 14.15 | 13.65 | 13.11 | 12.67 | 12.31 | 12.02 |
| 3 | 15.83 | 15.34 | 14.38 | 13.88 | 13.33 | 12.89 | 12.52 | 12.22 |
| 4 | 16.05 | 15.56 | 14.58 | 14.08 | 13.53 | 13.07 | 12.69 | 12.38 |
| 5 | 16.27 | 15.77 | 14.78 | 14.27 | 13.71 | 13.24 | 12.85 | 12.53 |
| 6 | 16.48 | 15.98 | 14.97 | 14.45 | 13.88 | 13.39 | 13.00 | 12.66 |
| 7 | 16.69 | 16.18 | 15.16 | 14.63 | 14.05 | 13.54 | 13.14 | 12.78 |
| 8 | 16.91 | 16.39 | 15.35 | 14.81 | 14.22 | 13.69 | 13.27 | 12.90 |
| <i>KOH</i> | | | | | | | | |
| 1 | 15.92 | 14.73 | 13.89 | 13.39 | 12.81 | 12.40 | 12.05 | 11.79 |
| 2 | 16.49 | 15.27 | 14.44 | 13.90 | 13.32 | 12.89 | 12.53 | 12.25 |
| 3 | 16.86 | 15.61 | 14.79 | 14.23 | 13.64 | 13.20 | 12.83 | 12.54 |
| 4 | 17.16 | 15.88 | 15.07 | 14.49 | 13.89 | 13.45 | 13.07 | 12.77 |
| 5 | 17.41 | 16.12 | 15.31 | 14.71 | 14.11 | 13.66 | 13.27 | 12.97 |
| 6 | 17.65 | 16.34 | 15.52 | 14.91 | 14.31 | 13.85 | 13.45 | 13.14 |
| 7 | 17.87 | 16.54 | 15.73 | 15.10 | 14.49 | 14.02 | 13.62 | 13.30 |
| 8 | 18.09 | 16.74 | 15.93 | 15.28 | 14.67 | 14.20 | 13.79 | 13.46 |

$\Delta_R G_T^\circ$ denotes the change in standard free energy for reaction (21) and is given as

$$\Delta_R G_T^\circ = b\Delta_f G_B^{\circ*} + c\Delta_f G_{H_2O}^{\circ*} - a\Delta_f G_A^{\circ*} - (x-z)\Delta_f G_{H^+}^{\circ*} - (z/2)\Delta_f G_{H_2}^{\circ*} \quad (24)$$

where $\Delta_f G_x^{\circ*}$ is the non-isothermal free energy of formation of component x at the temperature of interest. This quantity is defined in the following section.

Equation (22) can be expanded to yield

$$E = E^\circ + \frac{2.303RT}{zF} [a \log a_A - b \log a_B - c \log a_w] - \frac{2.303xRT}{zF} \text{pH} \quad (25)$$

For reactions in which no change of oxidation state occurs, $z = 0$ and reaction (21) reduces to



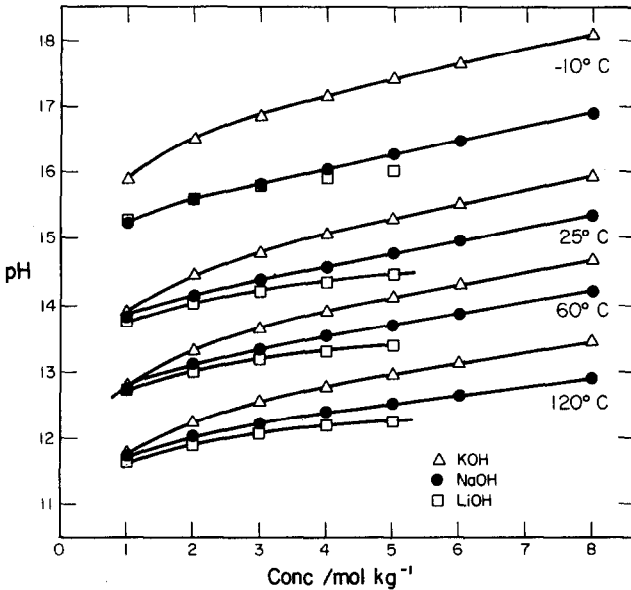


Fig. 3. Variation of pH with concentration for KOH, NaOH, and LiOH solutions as a function of temperature.

The equilibrium condition is therefore given as

$$xpH = -(\Delta_R G_T^\circ / 2.303RT) + a \log a_A - b \log a_B - c \log a_w \quad (27)$$

Potential-pH equations for various reactions of interest in the Li/H₂O, Al/H₂O, Zn/H₂O, Ni/H₂O, Fe/H₂O and O₂/H₂O systems were computed using a computer program, 'THERM'. This program was developed from a version [18] originally written to define the thermodynamics of metal/water systems under water-cooled, nuclear power plant conditions. The extended program has the facility for calculating the activity of water and the pH of each of the three hydroxide solutions. Using these data, it then computes the equilibrium potentials for each reaction at various stoichiometric concentrations of alkali hydroxide. The program is also capable of handling mixed oxidation products such as Ni(FeO₂)₂ or NaAlO₂. The former may be produced in an actual battery system due to transport of the soluble products from one electrode to the other. On the other hand, combination of the soluble species with an electrolyte cation will result in the second type of mixed product.

Evaluation of free energy functions

In order to obtain the potential-pH relationship for a reaction, a method is required for calculating the change in standard free energy at the temperature of interest. In this analysis, $\Delta_R G_T^\circ$ is evaluated from the non-isothermal free energies for the species involved in the reaction as defined by Macdonald and co-workers [19, 20]

$$\Delta_f G_T^{\circ*} = \Delta_f G_{298}^{\circ} - S_{298}^{\circ}(T - 298) - T \int_{298}^T (C_p^{\circ}/T) dT + \int_{298}^T C_p^{\circ} dT \quad (28)$$

where $\Delta_f G_{298}^{\circ}$ is the conventional isothermal free energy of formation at 298 K, S_{298}° is the absolute entropy at the reference temperature, and C_p° is the heat capacity, which is usually a function of temperature. The quantity $\Delta_f G_T^{\circ*}$ strictly refers to the free energy of formation of the compound at temperature T from its elements at 298 K. It therefore differs from the isothermal free energy of formation at elevated temperatures, which is based on the convention that the free energy of an element at all temperatures is zero. Both the non-isothermal and isothermal methods of calculation lead to identical results for $\Delta_R G_T^{\circ}$. However, the non-isothermal approach substantially reduces the number of calculations involved.

For non-dissolved species, accurate heat capacity functions of the form

$$C_p^{\circ} = A + BT + CT^{-2} \quad (29)$$

are commonly available. By contrast, there is a marked lack of directly-measured heat capacity data for dissolved ionic species. Consequently, it is usually necessary to estimate values for these species. The most widely used methods are the Criss-Cobble [21] "correspondence principle" and the linear ionic heat capacity (LIHC) approximation [10]. In the latter, the partial molal heat capacities for dissolved species are given in the form

$$\bar{C}_p^{\circ} = BT \quad (30)$$

The thermodynamic data used were taken whenever possible from the extensive compilation of Naumov *et al.* [10], and from various NBS [22] and U.S. Bureau of Mines [23] tabulations. Data that were taken or calculated from other sources are summarized in Table 8, together with appropriate references and comments on the methods of evaluation.

It should be noted that there are a number of cases, mainly among the dissolved species, for which neither directly-measured nor estimated (LIHC) heat capacity data are available. For these species, C_p° has been taken as zero. In general, when heat capacity data for dissolved species are known, the contribution to $\Delta_f G_T^{\circ*}$ from the two heat capacity terms in eqn. (28) is less than 1% for temperatures over the range 263 - 393 K. It is therefore assumed that where the C_p contribution is neglected, the error is sufficiently low to be acceptable in the present study.

Equilibrium potential/concentration data

Equilibrium potentials for selected reactions in the systems of interest were calculated by substitution of water activity and pH data into the appropriate potential-pH equations. Calculations were performed for stoichiometric alkali hydroxide concentrations over the range 1 - 8 mol kg⁻¹. For reactions which involve dissolved reactants or products, all ionic activities were arbitrarily set equal to 10⁻⁶ mol kg⁻¹ in accordance with normal practice [30]. This choice of activity will lead to an inherent error

TABLE 8

Thermodynamic data for species not listed in references 10, 22, and 23

| Species | $\Delta_f G_{298}^\circ$ (kJ mol ⁻¹) | S° ^a (J K ⁻¹ mol ⁻¹) | C_p° (J K ⁻¹ mol ⁻¹) | Comments |
|-----------------------------------|---|---|--|--|
| FeOOH | [10] | [10] | 70.12 | Calculated from "element additivity" ^b |
| FeO ₂ ²⁻ | -301.2 [24] | -98.16 | NDA ^c | Calculated using the method of Connick and Powell [25] |
| FeO ₄ ²⁻ | -467.4 | 10.79 | NDA | $\Delta_f G_{298}^\circ$ from Pourbaix [30] |
| Fe ²⁺ | -91.21 | -107 | NDA | |
| FeOH ⁺ | -274.26 | -33 | NDA | From Tremaine <i>et al.</i> [24] |
| HFeO ₂ ⁻ | -376.35 | 63 | NDA | |
| Fe(OH) ₂ (aq) | [10] | 50 | NDA | S° estimated from plot of S_n° vs. n for ions Fe(OH) _{<i>n</i>} ²⁻ⁿ |
| Ni(OH) ⁺ | -212.5 | -50 | 44.3 | Calculated from data of Tremaine [26] |
| Ni(OH) ₂ (aq) | -402.7 | -65.1 | 119.6 | |
| HNiO ₂ ⁻ | -348.3 | -214.1 | 119.6 | |
| Ni ₃ O ₄ | -712.1 | 149.2 | $129.035 + 0.7146 \times 10^{-1} T$ $- 0.2393 \times 10^7 T^{-2}$ | Cowan and Staehle [27] |
| NiOOH | -321.7 | 66.9 ₈ | 66.9 ₀ | S° and C_p° from "element additivity" ^b $\Delta_f G^\circ$ from $\Delta_f H^\circ$ and $\Delta_f S^\circ$ [28] |
| Ni ₂ O ₃ | -469.9 | 89.9 | $98.28 + 0.7782 \times 10^{-1} T$ $- 0.1485 \times 10^7 T^{-2}$ | Cowan and Staehle [27] |
| Zn(OH) ⁺ | -341.96 | 64.0 | 40.3 | Data taken from the compilation of Khodakovsky and Yelkin [29] |
| Zn(OH) ₂ (aq) | -525.09 | -25.5 | 115.5 | C_p° for ions computed from pK and Y's observation that $\Delta C_p^\circ = 0$ for ion hydrolysis |
| Zn(OH) ₃ | -696.64 | 64.9 | -32.9 ₉ | |
| Zn(OH) ₄ ²⁻ | -861.07 | 17.6 | -181.5 | |
| ZnO | -320.87 | 43.64 | [10] | |
| ϵ -Zn(OH) ₂ | -556.05 | 76.99 | [10] | |

^aEntropy on the conventional scale where $S_{H^+, 298}^\circ = 0$. The absolute entropies used in eqn. (28) are obtained from $S^\circ - 20.92z$, where z = ion charge including sign.

^bThe entropy and particularly the heat capacity of a compound $X_m Y_n$ can be estimated from that for a compound $X_{m'} Y_{n'}$ and for either element X or Y, provided that the compounds have coordination lattices. Thus, the heat capacity of X in the reference compound is $C_p(X, \text{ref}) = [C_p(X_{m'} Y_{n'}) - n' C_p(Y)]/m'$. The heat capacity of the unknown is therefore $C_p(X_m Y_n) = m C_p(X, \text{ref}) + n C_p(Y)$. This method has been applied successfully to estimating thermodynamic properties for the oxides of silver [20].

^cNDA — no data available.

in the potentials of electrodes such as the $\text{Zn}(\text{OH})_4^{2-}/\text{Zn}$ couple in battery systems which may involve quite high concentrations of soluble species. This error is specific to a particular battery system and appropriate corrections should be made when calculating cell voltage efficiencies.

Previous work [7] has shown that it is more convenient to plot the calculated equilibrium potentials against $\log m_{\text{MOH}}$, rather than pH_T as is more common. The E/pH_T plots are more complex in form than those involving $\log m_{\text{MOH}}$ owing to the variation of the activity of water and γ_{\pm} with composition. Even so, the $E/\log m_{\text{MOH}}$ plots still exhibit the effect of such variations in non-linear correlations as seen, for example, in Fig. 8.

The E versus $\log m_{\text{MOH}}$ diagrams for a given metal exhibit the same features for the three alkali metal hydroxides. Since KOH is commonly used as the electrolyte in alkaline batteries, only the diagrams for this hydroxide are presented here (Figs. 4 - 8). Data are shown only for the electrode reactions desired in battery systems, and various parasitic reactions that might occur. The desired reactions considered for the five metals were as follows:

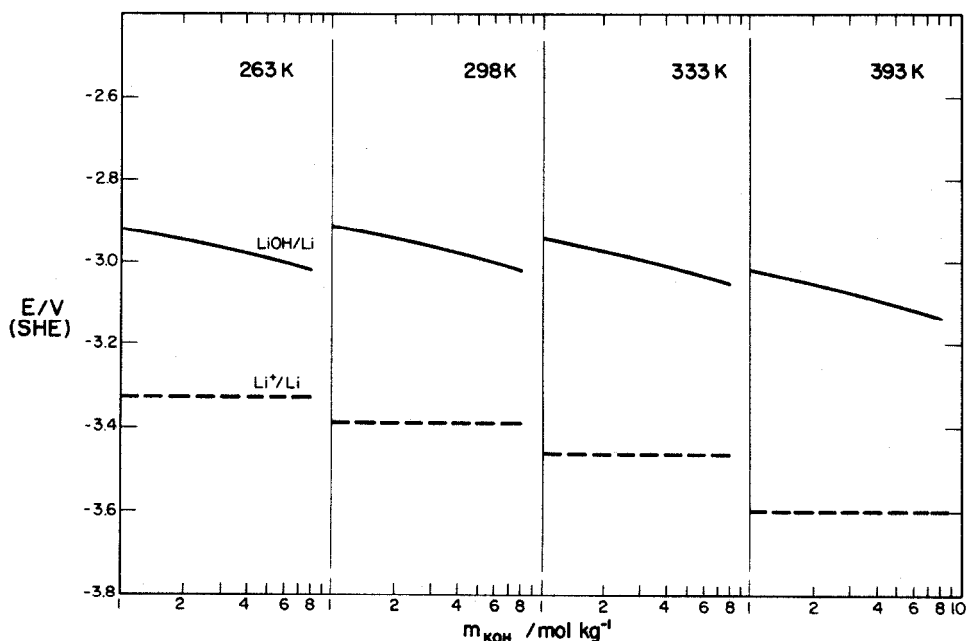


Fig. 4. Potential vs. $\log m_{\text{KOH}}$ diagrams for lithium in concentrated potassium hydroxide solutions as a function of temperature. $a_{\text{Li}^+} = 10^{-6} \text{ mol kg}^{-1}$.

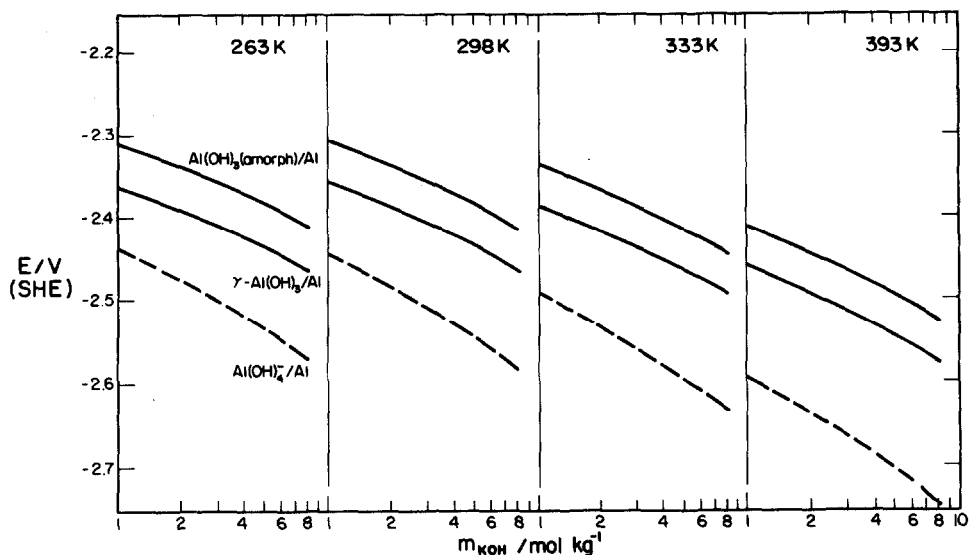


Fig. 5. Potential vs. $\log m_{\text{KOH}}$ diagrams for aluminum in concentrated potassium hydroxide solution as a function of temperature. $a_{\text{Al}(\text{OH})_4^-} = 10^{-6} \text{ mol kg}^{-1}$.

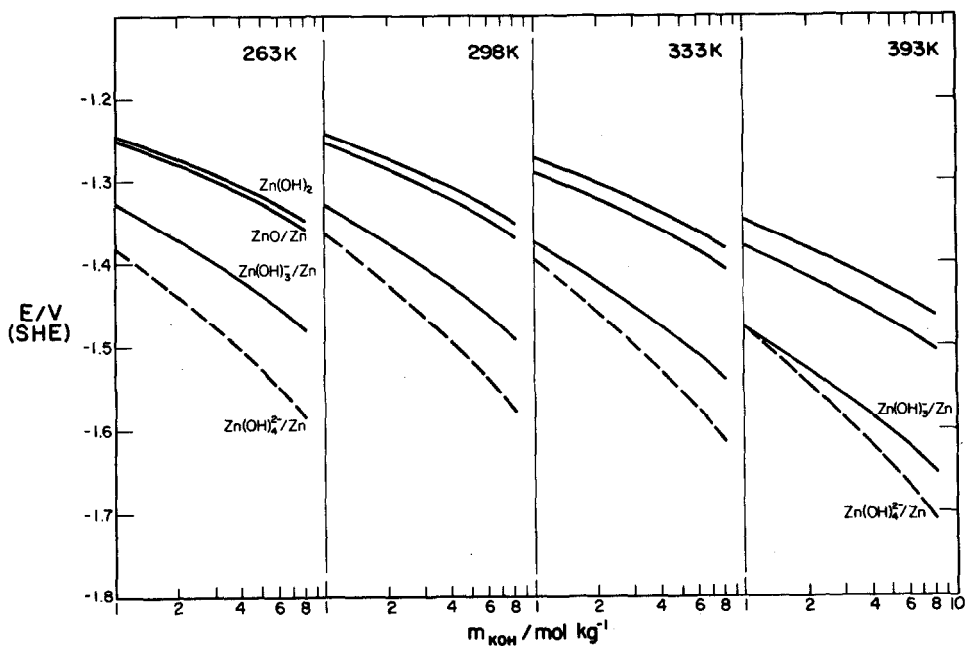


Fig. 6. Potential vs. $\log m_{\text{KOH}}$ diagrams for zinc in concentrated potassium hydroxide solution as a function of temperature. $a_{\text{Zn}(\text{OH})_3^-} = 10^{-6} \text{ mol kg}^{-1}$, $a_{\text{Zn}(\text{OH})_4^{2-}} = 10^{-6} \text{ mol kg}^{-1}$.

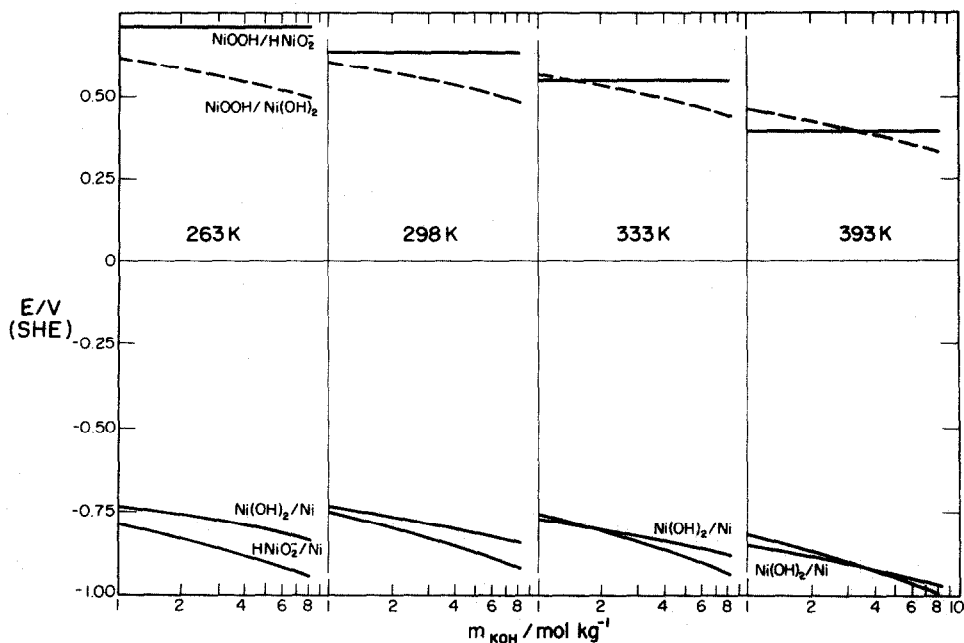


Fig. 7. Potential vs. $\log m_{\text{KOH}}$ diagrams for nickel in concentrated potassium hydroxide solution as a function of temperature. $a_{\text{HNiO}_2^-} = 10^{-6} \text{ mol kg}^{-1}$.

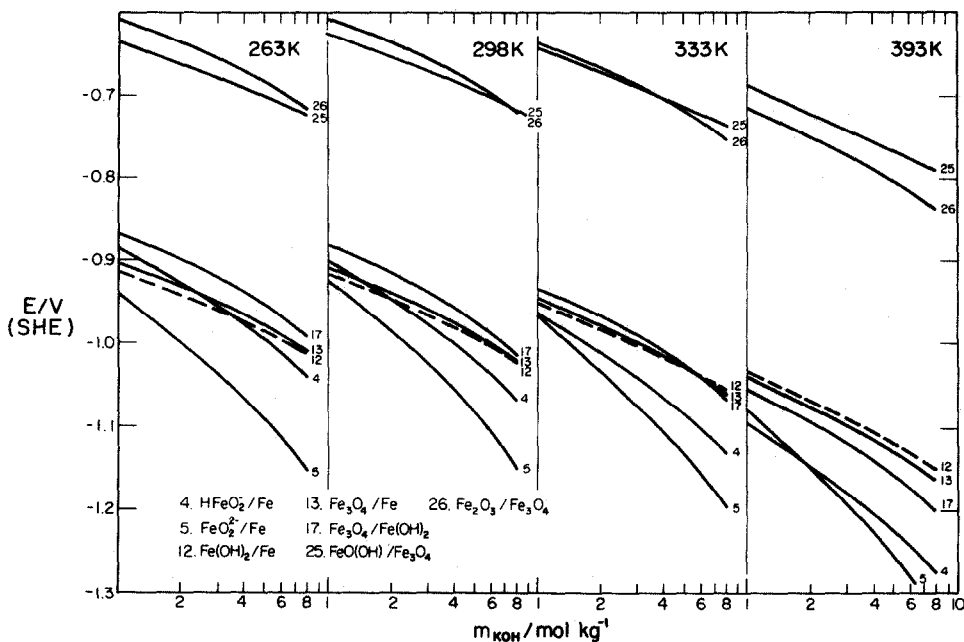
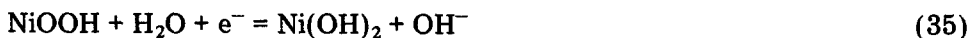


Fig. 8. Potential vs. $\log m_{\text{KOH}}$ diagram for iron in concentrated potassium hydroxide solution as a function of temperature. $a_{\text{HFeO}_2^-} = 10^{-6} \text{ mol kg}^{-1}$, $a_{\text{FeO}_2^{2-}} = 10^{-6} \text{ mol kg}^{-1}$.



In those instances where the reaction is a dissolution process, the parasitic reactions considered generally involve passivation, whereas for Ni and Fe, dissolution is a possibility. The broken line in each diagram represents the equilibrium potentials for the appropriate desired reaction. In the cases of Li, Al, and Zn, the thermodynamically-favoured reaction of the pure metal is the desired reaction, and the metal oxidizes directly to the pertinent species in the above reactions. The thermodynamically-favoured reaction for Fe, however, produces FeO_2^{2-} or, at 393 K, HFeO_2^- . The equilibrium potentials for the $\text{Fe}/\text{FeO}_2^{2-}$ and $\text{Fe}/\text{HFeO}_2^-$ couples were derived for an activity of 10^{-6} mol kg^{-1} for the oxyanions. In practice, the $\text{Fe}/\text{Fe(OH)}_2$ reaction would be favoured if the activities of FeO_2^{2-} and HFeO_2^- were sufficiently large or, more likely, the dissolution reactions were discounted for kinetic reasons.

In batteries with Ni electrodes, a $\text{Ni}/\text{Ni(OH)}_2$ couple is unsuitable as the Ni(OH)_2 cannot be easily reduced. Instead, the $\text{Ni(OH)}_2/\text{NiOOH}$ reaction is utilized.

The $E/\log m_{\text{MOH}}$ diagrams for Zn and Fe exhibit changes in the relative positions of the metal/anion equilibria curves with increasing temperature. The curves associated with HFeO_2^- and Zn(OH)_3^- move closer to those for FeO_2^{2-} and Zn(OH)_4^{2-} , respectively, with the two pairs of curves intersecting at 393 K. Therefore, each anion in both cases at this temperature is predominant over a part of the concentration range shown. In the case of Zn, the Zn(OH)_4^{2-} ion still prevails over most of that range but does so to a decreasing extent over the series $\text{KOH} > \text{NaOH} > \text{LiOH}$. The effect of temperature in the diagram for Fe is more marked such that at 393 K, HFeO_2^- replaces FeO_2^{2-} as the predominant anion for most of the concentration range. This change of anion reflects both a decrease in pK_a for HFeO_2^- and a lowering of the pH of the medium with increasing temperature.

Thermodynamics of alkaline batteries

Cell potentials

The alkaline batteries of practical interest can be separated into two broad groups:

- (i) metal/air systems where the metal can be Li, Al, Zn, and Fe;
- (ii) M/Ni systems where M = Fe, Zn, or H_2 .

The reactions considered to be taking place at the metal electrodes are given by eqns. (31) - (35) while the air and H_2 electrodes involve reactions (36) and (37), respectively.





Cell potentials for the above systems were calculated for each concentration and temperature: these are given in Tables 9 - 16. The cell potentials for the Al/air, Zn/air, and Zn/Ni systems were found to increase with concentration, where the magnitude of the increase over the range 1 - 5 mol kg⁻¹ follows the order KOH > NaOH > LiOH. By contrast, at each concentration the cell potentials decrease as the temperature increases.

Potentials for the Li/air, and to a lesser extent, the Fe/air cells exhibit the opposite behaviour. In the case of Li, the decrease in potential with concentration matches the change in the oxygen reduction potentials, since the Li anodic reaction is independent of pH. The decrease for Fe is due to a greater shift in the potential of the oxygen reduction reaction with concentration compared with that of the anodic reaction.

The cell potential data for the Fe/Ni system exhibit a different dependence on concentration and temperature from the previous two pairs of systems; an increase in either parameter in this case results in a decrease in

TABLE 9

Equilibrium potentials for Li/air cell in concentrated alkali hydroxide solutions ($P_{\text{O}_2} = 0.2$ atm, $a_{\text{Li}^+}(\text{NaOH, KOH}) = 10^{-6}$ mol kg⁻¹, $a_{\text{Li}^+}(\text{LiOH})$ is calculated for each m_{LiOH})

| m (mol kg ⁻¹) | Temperature (K) | | | | | | | |
|-----------------------------------|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 3.471 | 3.474 | 3.455 | 3.443 | 3.428 | 3.414 | 3.400 | 3.386 |
| 2 | 3.442 | 3.443 | 3.423 | 3.410 | 3.394 | 3.379 | 3.362 | 3.347 |
| 3 | 3.425 | 3.425 | 3.403 | 3.390 | 3.373 | 3.357 | 3.339 | 3.324 |
| 4 | 3.412 | 3.411 | 3.388 | 3.375 | 3.358 | 3.342 | 3.322 | 3.307 |
| 5 | 3.401 | 3.400 | 3.376 | 3.363 | 3.345 | 3.329 | 3.308 | 3.295 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 3.778 | 3.782 | 3.788 | 3.794 | 3.801 | 3.807 | 3.814 | 3.821 |
| 2 | 3.763 | 3.766 | 3.771 | 3.776 | 3.781 | 3.787 | 3.792 | 3.798 |
| 3 | 3.751 | 3.754 | 3.758 | 3.762 | 3.767 | 3.772 | 3.777 | 3.783 |
| 4 | 3.740 | 3.742 | 3.747 | 3.750 | 3.755 | 3.760 | 3.765 | 3.771 |
| 5 | 3.729 | 3.732 | 3.736 | 3.739 | 3.744 | 3.749 | 3.754 | 3.761 |
| 6 | 3.719 | 3.721 | 3.725 | 3.729 | 3.733 | 3.739 | 3.745 | 3.751 |
| 8 | 3.699 | 3.701 | 3.705 | 3.709 | 3.713 | 3.720 | 3.726 | 3.734 |
| <i>KOH</i> | | | | | | | | |
| 1 | 3.745 | 3.786 | 3.786 | 3.791 | 3.800 | 3.805 | 3.811 | 3.816 |
| 2 | 3.716 | 3.757 | 3.754 | 3.760 | 3.768 | 3.772 | 3.777 | 3.781 |
| 3 | 3.698 | 3.739 | 3.734 | 3.741 | 3.747 | 3.751 | 3.755 | 3.759 |
| 4 | 3.683 | 3.725 | 3.719 | 3.726 | 3.731 | 3.735 | 3.738 | 3.742 |
| 5 | 3.671 | 3.713 | 3.706 | 3.713 | 3.718 | 3.721 | 3.725 | 3.728 |
| 6 | 3.660 | 3.703 | 3.694 | 3.702 | 3.706 | 3.709 | 3.712 | 3.715 |
| 8 | 3.639 | 3.683 | 3.672 | 3.681 | 3.685 | 3.687 | 3.690 | 3.693 |

TABLE 10

Equilibrium potentials for Al/air cell in concentrated alkali hydroxide solutions ($P_{O_2} = 0.2$ atm, $a_{Al(OH)_4^-} = 10^{-6}$ mol kg⁻¹)

| <i>m</i> (mol kg ⁻¹) | Temperature (K) | | | | | | | |
|--|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 2.848 | 2.844 | 2.840 | 2.836 | 2.831 | 2.825 | 2.818 | 2.811 |
| 2 | 2.852 | 2.849 | 2.844 | 2.841 | 2.836 | 2.830 | 2.824 | 2.817 |
| 3 | 2.854 | 2.852 | 2.847 | 2.844 | 2.839 | 2.833 | 2.827 | 2.821 |
| 4 | 2.856 | 2.853 | 2.849 | 2.846 | 2.841 | 2.835 | 2.830 | 2.823 |
| 5 | 2.857 | 2.855 | 2.851 | 2.847 | 2.843 | 2.837 | 2.831 | 2.824 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 2.847 | 2.845 | 2.841 | 2.838 | 2.832 | 2.827 | 2.820 | 2.813 |
| 2 | 2.852 | 2.850 | 2.846 | 2.843 | 2.838 | 2.833 | 2.827 | 2.820 |
| 3 | 2.855 | 2.854 | 2.850 | 2.847 | 2.842 | 2.837 | 2.831 | 2.824 |
| 4 | 2.858 | 2.857 | 2.853 | 2.850 | 2.845 | 2.840 | 2.834 | 2.827 |
| 5 | 2.860 | 2.859 | 2.855 | 2.852 | 2.848 | 2.842 | 2.837 | 2.830 |
| 6 | 2.863 | 2.861 | 2.858 | 2.855 | 2.850 | 2.845 | 2.839 | 2.832 |
| 8 | 2.866 | 2.865 | 2.861 | 2.858 | 2.854 | 2.848 | 2.842 | 2.835 |
| <i>KOH</i> | | | | | | | | |
| 1 | 2.858 | 2.844 | 2.842 | 2.838 | 2.832 | 2.827 | 2.821 | 2.815 |
| 2 | 2.866 | 2.853 | 2.852 | 2.848 | 2.842 | 2.837 | 2.831 | 2.825 |
| 3 | 2.871 | 2.858 | 2.857 | 2.853 | 2.848 | 2.843 | 2.838 | 2.832 |
| 4 | 2.875 | 2.861 | 2.861 | 2.857 | 2.852 | 2.847 | 2.842 | 2.836 |
| 5 | 2.878 | 2.864 | 2.864 | 2.860 | 2.855 | 2.850 | 2.845 | 2.838 |
| 6 | 2.880 | 2.866 | 2.867 | 2.862 | 2.858 | 2.853 | 2.848 | 2.842 |
| 8 | 2.884 | 2.870 | 2.871 | 2.866 | 2.862 | 2.857 | 2.852 | 2.846 |

the cell potential. The concentration effect, which is small, arises simply from the decrease in the activity of water.

The potential of an H₂/Ni cell is, of course, strongly dependent on the partial pressure of H₂ and this value reflects the state of charge of the cell. Accordingly, cell potential data were calculated for the charged and the discharged states. For the charged condition, P_{H_2} was arbitrarily taken as 100 atm, while for the discharged condition P_{H_2} was assumed to be 1 atm. As expected, $E_R(\text{charged})$ is greater than $E_R(\text{discharged})$, with the difference increasing with temperature. For both conditions, however, E_R is independent of the stoichiometric concentration, and therefore pH, since the pH contributions to the two electrode potentials compensate each other.

Efficiencies

The calculated cell potentials can be used in conjunction with available test data to estimate the efficiencies of the appropriate battery systems. The voltage efficiency of a cell at open circuit can be defined according to eqn. (3) as

TABLE 11

Equilibrium potentials for Zn/air cell in concentrated alkali hydroxide solutions ($P_{O_2} = 0.2$ atm, $a_{Zn(OH)_4^{2-}} = 10^{-6}$ mol kg⁻¹)

| <i>m</i> (mol kg ⁻¹) | Temperature (K) | | | | | | | |
|--|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 1.773 | 1.764 | 1.754 | 1.746 | 1.734 | 1.719 | 1.703 | 1.685 |
| 2 | 1.787 | 1.779 | 1.769 | 1.762 | 1.750 | 1.736 | 1.721 | 1.704 |
| 3 | 1.795 | 1.788 | 1.778 | 1.771 | 1.760 | 1.746 | 1.732 | 1.715 |
| 4 | 1.801 | 1.794 | 1.785 | 1.778 | 1.766 | 1.753 | 1.739 | 1.722 |
| 5 | 1.805 | 1.799 | 1.790 | 1.783 | 1.772 | 1.759 | 1.745 | 1.728 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 1.772 | 1.768 | 1.759 | 1.750 | 1.738 | 1.724 | 1.709 | 1.692 |
| 2 | 1.786 | 1.783 | 1.775 | 1.767 | 1.756 | 1.744 | 1.729 | 1.713 |
| 3 | 1.797 | 1.794 | 1.787 | 1.780 | 1.769 | 1.757 | 1.743 | 1.727 |
| 4 | 1.807 | 1.804 | 1.797 | 1.790 | 1.780 | 1.768 | 1.753 | 1.737 |
| 5 | 1.816 | 1.813 | 1.807 | 1.800 | 1.790 | 1.777 | 1.763 | 1.746 |
| 6 | 1.824 | 1.822 | 1.815 | 1.808 | 1.798 | 1.785 | 1.771 | 1.754 |
| 8 | 1.840 | 1.837 | 1.831 | 1.824 | 1.814 | 1.800 | 1.785 | 1.767 |
| <i>KOH</i> | | | | | | | | |
| 1 | 1.804 | 1.764 | 1.761 | 1.753 | 1.738 | 1.726 | 1.711 | 1.696 |
| 2 | 1.831 | 1.791 | 1.791 | 1.782 | 1.769 | 1.758 | 1.744 | 1.730 |
| 3 | 1.848 | 1.808 | 1.810 | 1.800 | 1.788 | 1.777 | 1.764 | 1.750 |
| 4 | 1.861 | 1.820 | 1.823 | 1.813 | 1.802 | 1.791 | 1.778 | 1.765 |
| 5 | 1.872 | 1.830 | 1.834 | 1.824 | 1.813 | 1.803 | 1.790 | 1.777 |
| 6 | 1.881 | 1.839 | 1.844 | 1.834 | 1.823 | 1.813 | 1.800 | 1.787 |
| 8 | 1.897 | 1.854 | 1.861 | 1.850 | 1.840 | 1.830 | 1.818 | 1.804 |

$$\epsilon_{V_o} = \frac{E_{test}}{E_R} \quad (38)$$

where E_{test} is the open-circuit potential for a practical cell and E_R is the computed thermodynamic value. An evaluation of the coulombic efficiencies would require a knowledge of the charge/discharge characteristics for the battery system.

The voltage efficiencies of several systems at open-circuit are given in Table 17. In most cases, the potentials of test cells, E_{test} , have been obtained by extrapolation and reading of plotted data, and therefore they are not exact values. In general, the efficiencies of the test cells listed are found to lie between 90 and 100%. This is a very significant feature since it implies that, at least at open-circuit, there is little, if any, contribution from parasitic redox couples to the cell potentials for these systems. The efficiency of the Zn/Ni battery is unexpectedly low, particularly for the 50 A h cell. It should be noted, however, that the value of E_R , and therefore the efficiency of the Zn/Ni system, was obtained assuming $a(Zn(OH)_4^{2-}) = 10^{-6}$

TABLE 12

Equilibrium potentials for the Fe/air cell in concentrated alkali hydroxide solutions ($P_{O_2} = 0.2$ atm)

| m (mol kg^{-1}) | Temperature (K) | | | | | | | |
|----------------------------|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 1.334 | 1.329 | 1.314 | 1.305 | 1.293 | 1.281 | 1.268 | 1.255 |
| 2 | 1.334 | 1.328 | 1.314 | 1.305 | 1.293 | 1.281 | 1.268 | 1.255 |
| 3 | 1.334 | 1.328 | 1.313 | 1.304 | 1.292 | 1.280 | 1.267 | 1.254 |
| 4 | 1.333 | 1.328 | 1.313 | 1.304 | 1.292 | 1.279 | 1.267 | 1.254 |
| 5 | 1.333 | 1.327 | 1.313 | 1.304 | 1.291 | 1.279 | 1.266 | 1.253 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 1.334 | 1.329 | 1.314 | 1.305 | 1.293 | 1.281 | 1.268 | 1.255 |
| 2 | 1.334 | 1.328 | 1.314 | 1.305 | 1.293 | 1.280 | 1.268 | 1.255 |
| 3 | 1.334 | 1.328 | 1.313 | 1.304 | 1.292 | 1.280 | 1.267 | 1.254 |
| 4 | 1.333 | 1.327 | 1.313 | 1.303 | 1.291 | 1.279 | 1.266 | 1.253 |
| 5 | 1.332 | 1.326 | 1.312 | 1.303 | 1.290 | 1.278 | 1.265 | 1.253 |
| 6 | 1.331 | 1.325 | 1.311 | 1.302 | 1.290 | 1.277 | 1.265 | 1.252 |
| 8 | 1.329 | 1.323 | 1.309 | 1.300 | 1.287 | 1.275 | 1.262 | 1.250 |
| <i>KOH</i> | | | | | | | | |
| 1 | 1.334 | 1.329 | 1.314 | 1.305 | 1.293 | 1.281 | 1.268 | 1.255 |
| 2 | 1.333 | 1.328 | 1.313 | 1.305 | 1.292 | 1.280 | 1.267 | 1.254 |
| 3 | 1.332 | 1.327 | 1.313 | 1.304 | 1.291 | 1.279 | 1.266 | 1.253 |
| 4 | 1.332 | 1.327 | 1.312 | 1.303 | 1.290 | 1.278 | 1.265 | 1.252 |
| 5 | 1.331 | 1.326 | 1.311 | 1.302 | 1.290 | 1.277 | 1.264 | 1.251 |
| 6 | 1.330 | 1.325 | 1.310 | 1.301 | 1.288 | 1.276 | 1.263 | 1.250 |
| 8 | 1.327 | 1.322 | 1.307 | 1.298 | 1.286 | 1.273 | 1.261 | 1.248 |

mol kg^{-1} . The use of a higher activity would give a lower E_R , thereby leading to an improvement in the apparent voltage efficiency.

Finally, measured potentials of several electrodes are compared with calculated equilibrium values in Table 18. In the case of Li, the open-circuit potential is more positive than the equilibrium potential for the Li/Li⁺ couple as a result of corrosion [35]. Nevertheless, the corrosion potential lies much closer to the potential for the Li/Li⁺ couple than that for the H₂O/H₂ couple. This feature indicates that the H₂O reduction is substantially polarised, as noted in earlier work [35], and is therefore the rate-controlling step in the corrosion of Li.

Using polarization data measured previously [32] for the Fe and air electrodes, the open-circuit potentials were obtained by extrapolation to zero current. The open-circuit potential for the Fe electrode is shown to be more positive than the equilibrium potential for the Fe/Fe(OH)₂ couple. The air electrode, however, exhibits an open-circuit potential which is considerably less positive than the O₂/H₂O equilibrium potential. These differences would account for the relatively low voltage efficiency found

TABLE 13

Equilibrium potentials for Ni/Zn cell in concentrated alkali hydroxide solutions
($a_{\text{Zn}(\text{OH})_4^{2-}} = 10^{-6} \text{ mol kg}^{-1}$)

| <i>m</i> (mol kg ⁻¹) | Temperature (K) | | | | | | | |
|--|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 1.962 | 1.958 | 1.958 | 1.956 | 1.952 | 1.945 | 1.936 | 1.926 |
| 2 | 1.975 | 1.972 | 1.973 | 1.971 | 1.968 | 1.961 | 1.953 | 1.944 |
| 3 | 1.983 | 1.980 | 1.981 | 1.980 | 1.977 | 1.971 | 1.964 | 1.954 |
| 4 | 1.988 | 1.986 | 1.988 | 1.987 | 1.983 | 1.977 | 1.971 | 1.961 |
| 5 | 1.992 | 1.990 | 1.992 | 1.992 | 1.988 | 1.983 | 1.977 | 1.966 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 1.961 | 1.961 | 1.963 | 1.960 | 1.956 | 1.950 | 1.942 | 1.932 |
| 2 | 1.975 | 1.976 | 1.979 | 1.977 | 1.974 | 1.969 | 1.962 | 1.952 |
| 3 | 1.985 | 1.987 | 1.990 | 1.989 | 1.986 | 1.981 | 1.975 | 1.965 |
| 4 | 1.994 | 1.996 | 2.000 | 1.999 | 1.996 | 1.991 | 1.985 | 1.975 |
| 5 | 2.002 | 2.004 | 2.008 | 2.007 | 2.005 | 2.000 | 1.993 | 1.983 |
| 6 | 2.010 | 2.012 | 2.016 | 2.015 | 2.013 | 2.007 | 2.000 | 1.990 |
| 8 | 2.023 | 2.025 | 2.029 | 2.028 | 2.026 | 2.020 | 2.012 | 2.002 |
| <i>KOH</i> | | | | | | | | |
| 1 | 1.992 | 1.957 | 1.965 | 1.963 | 1.956 | 1.952 | 1.944 | 1.936 |
| 2 | 2.019 | 1.984 | 1.994 | 1.991 | 1.986 | 1.982 | 1.976 | 1.969 |
| 3 | 2.035 | 1.999 | 2.012 | 2.009 | 2.004 | 2.001 | 1.995 | 1.988 |
| 4 | 2.047 | 2.011 | 2.025 | 2.021 | 2.017 | 2.014 | 2.009 | 2.002 |
| 5 | 2.056 | 2.020 | 2.035 | 2.031 | 2.028 | 2.025 | 2.019 | 2.013 |
| 6 | 2.065 | 2.028 | 2.043 | 2.039 | 2.036 | 2.034 | 2.028 | 2.022 |
| 8 | 2.078 | 2.041 | 2.058 | 2.053 | 2.051 | 2.048 | 2.043 | 2.037 |

(Table 17) for the Fe/air battery and, furthermore, imply that the major part of the loss in performance is associated with the air electrode. In practice, however, H_2O_2 may be the reaction product at the air electrode, and the potential is therefore determined by the $\text{O}_2/\text{H}_2\text{O}_2$ couple.

Uncertainties in the data base

It was apparent, when evaluating published data for the properties of concentrated alkaline solutions, that the calculated equilibrium potentials may be subject to considerable error. The principal sources of error are considered to be:

(i) Uncertainty in the activity of water, particularly in the case of concentrated KOH solutions.

(ii) Uncertainty in the dissociation constant for water in concentrated alkaline solutions. This quantity is used to estimate the pH (see eqn. (14)) but is available only for dilute aqueous solutions (*e.g.*, $< 1 \text{ mol kg}^{-1}$ KCl) over the temperature range of interest.

TABLE 14

Equilibrium potentials for Ni/Fe cell in concentrated alkali hydroxide solutions

| <i>m</i> (mol kg ⁻¹) | Temperature (K) | | | | | | | |
|--|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 1.523 | 1.522 | 1.518 | 1.515 | 1.511 | 1.507 | 1.501 | 1.495 |
| 2 | 1.522 | 1.521 | 1.517 | 1.515 | 1.511 | 1.506 | 1.500 | 1.494 |
| 3 | 1.522 | 1.520 | 1.517 | 1.514 | 1.510 | 1.505 | 1.499 | 1.493 |
| 4 | 1.521 | 1.520 | 1.516 | 1.513 | 1.509 | 1.504 | 1.498 | 1.492 |
| 5 | 1.520 | 1.519 | 1.515 | 1.512 | 1.508 | 1.503 | 1.497 | 1.491 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 1.523 | 1.522 | 1.518 | 1.515 | 1.511 | 1.506 | 1.501 | 1.495 |
| 2 | 1.522 | 1.521 | 1.517 | 1.515 | 1.510 | 1.505 | 1.500 | 1.494 |
| 3 | 1.521 | 1.520 | 1.516 | 1.513 | 1.509 | 1.504 | 1.499 | 1.493 |
| 4 | 1.520 | 1.519 | 1.515 | 1.512 | 1.508 | 1.503 | 1.497 | 1.491 |
| 5 | 1.518 | 1.517 | 1.513 | 1.510 | 1.506 | 1.501 | 1.496 | 1.490 |
| 6 | 1.517 | 1.515 | 1.511 | 1.508 | 1.504 | 1.500 | 1.494 | 1.488 |
| 8 | 1.512 | 1.511 | 1.507 | 1.504 | 1.500 | 1.495 | 1.490 | 1.484 |
| <i>KOH</i> | | | | | | | | |
| 1 | 1.522 | 1.522 | 1.518 | 1.515 | 1.511 | 1.506 | 1.501 | 1.495 |
| 2 | 1.521 | 1.521 | 1.516 | 1.514 | 1.510 | 1.505 | 1.499 | 1.493 |
| 3 | 1.519 | 1.519 | 1.515 | 1.512 | 1.508 | 1.503 | 1.497 | 1.491 |
| 4 | 1.517 | 1.517 | 1.513 | 1.510 | 1.506 | 1.501 | 1.496 | 1.489 |
| 5 | 1.516 | 1.516 | 1.511 | 1.508 | 1.504 | 1.499 | 1.493 | 1.487 |
| 6 | 1.514 | 1.514 | 1.509 | 1.506 | 1.502 | 1.497 | 1.491 | 1.485 |
| 8 | 1.509 | 1.509 | 1.504 | 1.502 | 1.497 | 1.492 | 1.486 | 1.480 |

(iii) Uncertainty in the degree of association of cations with hydroxide ions in the concentrated alkaline solutions. This is of no consequence for the calculation of pH because of the use of the "lever rule" (eqn. (16)), but will be important when calculating separately either the concentration or activity coefficient of the hydroxide ion.

(iv) Some uncertainty exists in the thermodynamic data base for the dissolved oxidation products of Fe, Ni, Zn, and Al, particularly in the Gibbs energies of formation and heat capacities. These data directly affect the precision of the calculated equilibrium potentials for the metal dissolution reactions and, hence, the cell potentials for certain equilibrium cells.

The sources of errors identified above all contribute to the uncertainty in the calculated cell potentials and voltage efficiencies although the magnitude of the overall error is clearly dependent on the particular system.

TABLE 15

Equilibrium potentials for Ni/H₂ cell in concentrated alkali hydroxide solutions (discharged condition, P_{H_2} assumed to be 1 atm)

| m (mol kg ⁻¹) | Temperature (K) | | | | | | | |
|-----------------------------------|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 2 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 3 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 4 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 5 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 2 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 3 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 4 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 5 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 6 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 8 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| <i>KOH</i> | | | | | | | | |
| 1 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 2 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 3 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 4 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 5 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 6 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |
| 8 | 1.439 | 1.435 | 1.423 | 1.416 | 1.407 | 1.397 | 1.388 | 1.378 |

Conclusion

(i) The good agreement between the calculated and published data for the activity coefficient of the hydroxide ion for LiOH, and to a lesser extent for NaOH, indicates that the thermodynamic calculations used to obtain γ_{\pm} are sufficiently reliable. The poorer agreement between the γ_{\pm} data for KOH may be attributable, at least in part, to inadequate data on the water activity.

(ii) The properties of the alkali metal hydroxide solutions are very dependent on temperature and concentration of MOH. In particular, the activity of water decreases markedly with increasing concentration, while the dependence of $\log \gamma_{\pm}$ on concentration varies with the cation. The pH also depends on the cation and increases along the series LiOH < NaOH < KOH.

(iii) The thermodynamically-favoured reaction of the pure metal in the case of Li, Al, and Zn is also the desired reaction for the particular

TABLE 16

Equilibrium potentials for Ni/H₂ cell in concentrated alkali hydroxide solutions (charged condition, P_{H_2} assumed to be 100 atm)

| m (mol kg ⁻¹) | Temperature (K) | | | | | | | |
|-----------------------------------|-----------------|-------|-------|-------|-------|-------|-------|-------|
| | 263 | 273 | 298 | 313 | 333 | 353 | 373 | 393 |
| <i>LiOH</i> | | | | | | | | |
| 1 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 2 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 3 | 1.491 | 1.489 | 1.482 | 1.478 | 1.478 | 1.467 | 1.462 | 1.456 |
| 4 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 5 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| <i>NaOH</i> | | | | | | | | |
| 1 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 2 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 3 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 4 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 5 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 6 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 8 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| <i>KOH</i> | | | | | | | | |
| 1 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 2 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 3 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 4 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 5 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 6 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |
| 8 | 1.491 | 1.489 | 1.482 | 1.478 | 1.473 | 1.467 | 1.462 | 1.456 |

battery. The thermodynamically least stable product for Fe is FeO_2^{2-} or, at 393 K, HFeO_2^- . The $\text{Fe}/\text{Fe}(\text{OH})_2$ reaction would be favoured if the activities of FeO_2^{2-} and HFeO_2^- were sufficiently large or the dissolution reactions were discounted for kinetic reasons.

(iv) The relative stabilities of the respective anions for iron (FeO_2^{2-} , HFeO_2^-) and zinc ($\text{Zn}(\text{OH})_3^-$, $\text{Zn}(\text{OH})_4^{2-}$) depend on temperature such that, at 393 K, each anion in both cases is predominant over a part of the concentration range 1 - 8 mol kg⁻¹.

(v) The variation of cell potentials with concentration of MOH and temperature depends on the particular battery. The calculated potentials of the Al/air, Zn/air, and Zn/Ni increase with concentration but decrease as the temperature increases. The Li/air, and to a lesser extent, the Fe/air cell potentials exhibit the opposite behaviour, whereas those for the Fe/Ni system decrease with an increase in either concentration or temperature. By contrast, the potentials of the H₂/Ni cell are independent of stoichiometric concentration, and therefore of the pH of the electrolyte.

TABLE 17

Voltage efficiencies of practical battery systems at open circuit

| System | Ref. | Conditions* | Features** | E_{test} (V) | E_{R} (V) | ϵ_{V_0} (%) |
|-------------------|--------|---|---|--------------------------|-----------------------|-------------------------|
| Ni/H ₂ | 31 | 30 wt.% KOH, 20 °C | P_{H_2} (initial) = 54 atm | 1.46 - 1.47 | 1.474 | 99 - 100 |
| | | 8.4 A, 7.7 A h charge | P_{H_2} (final) = 36 atm | 1.34 | 1.461 | 91 |
| Fe/air | 32 | 25 wt.% KOH + 15 g/l LiOH, 44 °C, charged at 12.5 mA cm ⁻² for 8 h | Cell #30, Cycle 20, 100 cm ² electrodes | 0.94 | 1.301 | 72 |
| Ni/Fe | 32 | 25 wt.% KOH, charged at 83.3 A/4 h | Discharged at 41.7 A, | 1.43 - 1.48 | 1.509 | 95 - 98 |
| | | | 83.3 A | 1.34 - 1.39 | | 89 - 92 |
| Ni/Zn | 33, 34 | 25 wt.% KOH | 50 A h cell, | 1.70 | 2.043 | 83 |
| | | | 225 A h cell | 1.83 | | 90 |

*The temperature was taken as 25 °C where not specified. For the Ni/H₂ and Fe/air cells, the values of E_{R} shown are for 25 °C and 40 °C, respectively.

**Ni/H₂: The hydrogen partial pressures given are the initial and final values for an open-circuit stand of 91.5 h.

Ni/Fe: The values of E_{test} shown cover a range of cells and cycle numbers.

N.B. While the authors realise that nominal capacity values would make the charging conditions more meaningful they regret that the information was not available. Nevertheless the comparative data given are still valid.

TABLE 18

Comparison of open circuit electrode potentials, E_{oc} with equilibrium potentials, E

| Electrode | Ref. | Conditions | Couple | E (V) | E_{oc} (V) |
|-----------|------|-------------------------------------|--|--|------------------------|
| Li | 35 | 4.5 M LiOH, 25 °C | Li ⁺ /Li H ₂ O/H ₂ | -3.010 ^a -0.855 ^b | -2.88 |
| Fe | 32 | 25 wt.% KOH + 15 g/l LiOH, 40 °C | Fe(OH) ₂ /Fe | -1.016 | -0.95 |
| Air | 32 | 25 wt.% KOH + 15 g/l LiOH, 40 °C | O ₂ /H ₂ O ^c | 0.285 | 0.0 |

^aFor the purpose of this comparison, $E_{\text{Li}^+/\text{Li}}$ for 5 m was considered to be adequate.

^bThe H₂ partial pressure was taken as 1 atm. A lower pressure would result in a more positive value of $E_{\text{H}_2\text{O}/\text{H}_2}$.

^cA four electron reaction is assumed. However, the reaction product at the air electrode may be H₂O₂.

(vi) Efficiencies of H₂/Ni, Fe/Ni, and Zn/Ni test cells at open-circuit lie between 90 and 100%, implying that there is little, if any, contribution from parasitic redox couples to the open-circuit cell potentials.

(vii) The relatively low efficiency of an Fe/air test battery is associated with the air electrode, suggesting that the potential of this electrode may be determined by the O₂/H₂O₂ couple.

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List of symbols

| | |
|----------------|--|
| a | Activity |
| a_w | Activity of water |
| A, A_m' | Debye-Huckel coefficients |
| C_p | Molar heat capacity (J K ⁻¹ mol ⁻¹) |
| d_0 | Density of solvent (g cm ⁻³) |
| D | Dielectric constant |
| E | Equilibrium potential (V) |
| E_c | Cell voltage (V) |
| E° | Standard electrode potential (V) |
| E_R | Reversible potential of a cell (V) |
| E_{test} | Open-circuit potential of a practical cell (V) |
| F | Faraday constant = 96 487 C eq ⁻¹ |
| ΔG | Molar free energy change (kJ mol ⁻¹) |
| $\Delta_f G^*$ | Non-isothermal free energy of formation of a species (kJ mol ⁻¹) |
| $\Delta_R G_T$ | Free energy change for a reaction at temperature T (kJ) |
| ΔH | Molar enthalpy change (kJ mol ⁻¹) |
| K_w | Dissociation constant of water |
| M | Molecular weight |
| m | Molality (mol kg ⁻¹) |
| n | Stoichiometric number of electrons in a cell reaction |
| p, p° | Vapor pressure of a solution and pure water, respectively (atm) |
| q | Total charge (C) |
| Q_w | Ionic product of water |
| S | Molar entropy (J K ⁻¹ mol ⁻¹) |
| T | Temperature (K) |
| z | Number of electrons in half-cell reaction |
| α | Charge (C) |

| | |
|------------------|---|
| γ_{\pm} | Stoichiometric mean molal activity coefficient |
| γ_{\pm}^* | Mean ionic activity coefficient |
| ϵ | Overall efficiency |
| ϵ_c | Coulombic efficiency |
| ϵ_T | Thermal efficiency |
| ϵ_V | Voltage efficiency |
| ν | Number of ions formed by electrolyte dissociation |
| ϕ | Osmotic coefficient |

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