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Authors

Bernardi, D.
Pawlikowski, E.
Newman, J.

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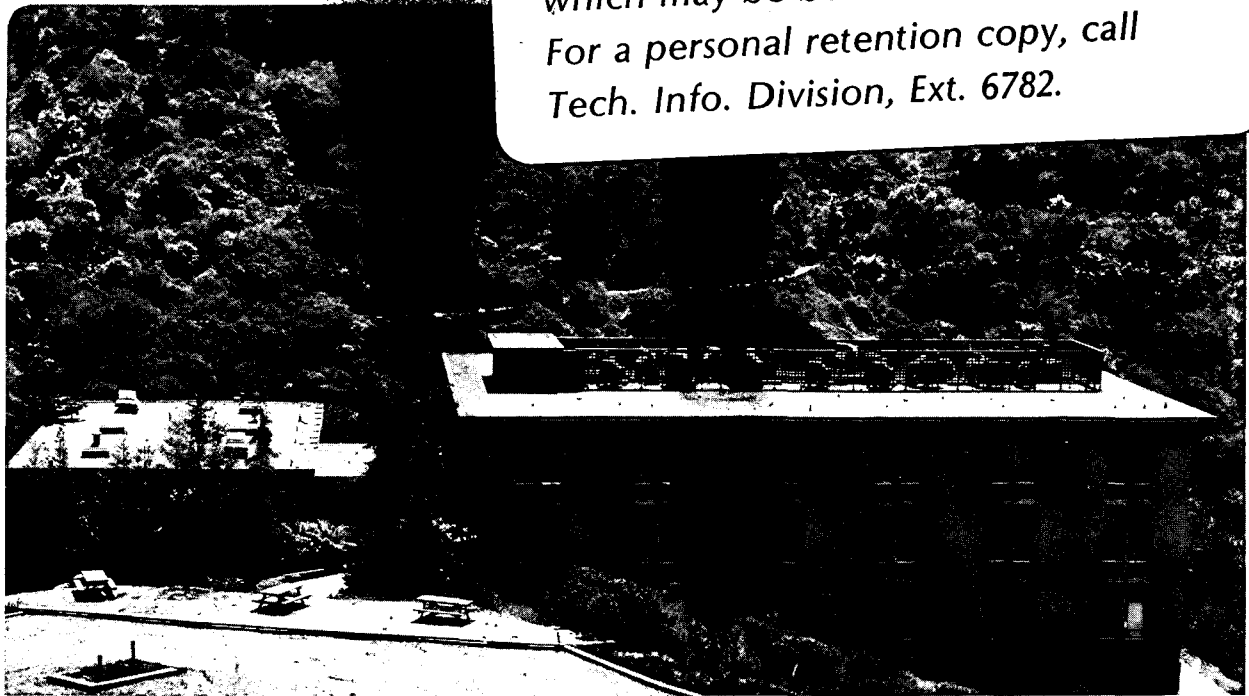
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D. Bernardi, E. Pawlikowski, and J. Newman

April 1984

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**A General Energy Balance for
Battery Systems**

Dawn Bernardi, Ellen Pawlikowski, and John Newman

**Materials and Molecular Research Division
Lawrence Berkeley Laboratory, and
Department of Chemical Engineering
University of California
Berkeley, California 94720**

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Abstract

A general energy balance for battery systems has been developed. This equation is useful for estimating cell thermal characteristics. Reliable predictions of cell temperature and heat generation rate are required for the design and thermal management of battery systems. The temperature of a cell changes as a result of electrochemical reactions, phase changes, mixing effects, and joule heating. The equation developed incorporates these effects in a complete and general manner. Simplifications and special cases are discussed. The results of applying the energy balance to a mathematical model of the LiAl/FeS cell discharged through two different reaction mechanisms are given as examples. The examples illustrate how the energy equation may be applied to a specific system to examine the relative contributions corresponding to the terms in the equation. The examples show that the processes involved in cell heat generation may be complex and that the application of a sufficiently general energy equation is advantageous.

Key descriptors: Battery, Thermodynamics, Energy Transfer, Enthalpy

Introduction

Energy balance calculations are required for the design and thermal management of battery systems. A proper cell energy balance will give reliable predictions of thermal characteristics such as heat generation and temperature-time profiles. In this work, we present a general energy balance equation for battery systems. This equation includes energy contributions from mixing, phase changes, and simultaneous electrochemical reactions with composition dependent open-circuit potentials. Such a thorough treatment has not appeared in the literature.

The problem of determining heat effects with simultaneous electrochemical reactions was first addressed by Sherfey and Brenner in 1958.^[1] The authors presented an equation for the rate of thermal energy generation in terms of the current fraction, the entropy change, and the overpotential for each reaction. Later, Gross^[2] presented essentially the same equation; however, he introduced a quantity for each reaction called the enthalpy voltage. The enthalpy voltage is the enthalpy of reaction per coulomb of charge, and it may be derived from the overpotential and the entropy change terms in Sherfey and Brenner's equation. These treatments are restricted in their application to cell reactions in which every reactant is present in a single, pure phase. Gibbard^[3] discussed the calculation of thermodynamic properties of battery systems when some of the reactants are dissolved in solution; however, his treatment of the energy balance considers the case of a single reaction without mixing effects.

Numerous researchers^[1,2,4-7,12] have adopted experimental approaches and used calorimetry to determine heat output directly. Dibrov and Bykov^[5] used calorimetric data along with enthalpy voltages to determine current fractions of the reactions of cadmium-silver oxide and zinc-silver oxide cells.

The formulation of a general energy balance is useful in developing a fundamental understanding of the processes involved in cell heat generation. However, in its most rigorous form, the energy balance presented is difficult to apply without a detailed mathematical model because instantaneous composition profiles and current fractions are required. For example, Tiedemann and Newman [8] have developed such a model for the lead-acid cell. A model for the lithium-aluminum, iron sulfide battery was presented by Pollard and Newman. [9,10] These models do provide the necessary information to calculate the thermal characteristics from an energy balance such as the one presented in this work; however, these works utilize a relatively simple energy equation in which mixing effects are ignored and a single cell reaction occurs. Pollard's model calculates current fractions of the two simultaneously occurring reactions, but the fractions are not utilized in the energy balance. In practice, it is difficult to obtain concentration profiles and to predict the partitioning of current among possible reactions. However, applying an energy equation that includes the effects of simultaneous reactions to experimental measurements will allow the calculation of the current fractions. In this work, simplifications and special cases of the general energy equation are discussed. The results of applying the energy balance to a mathematical model of the LiAl/LiCl-KCl/FeS cell are given as examples. The relative contributions corresponding to the terms in the equation are examined.

The Energy Balance

In this section, the general energy balance for a battery system will be derived. The temperature of the battery is assumed to be uniform throughout and changes with time as determined by the following processes:

- (1) reversible effects.
- (2) changes in the heat capacity of the system.
- (3) phase changes.
- (4) mixing effects.
- (5) joule heating.
- (6) heat transfer with the surroundings.

A battery may be thought of as a composite of many discrete phases that are changing in energy content. It is assumed that these phases are interacting by way of electrochemical reactions, phase changes, and mixing processes. The first law of thermodynamics may be written as

$$\frac{\partial H_{tot}}{\partial t} = q - IV, \quad (1)$$

where H_{tot} is the sum of the enthalpies of the phases expressed as

$$H_{tot} = \sum_j \int_{v_j} \left[\sum_i c_{i,j} \bar{H}_{i,j} \right] dv_j, \quad (2)$$

and i and j denote the individual species and phase, respectively. It is convenient to define an average composition for each of these phases and write

$\frac{\partial H_{tot}}{\partial t}$ as

$$\frac{\partial H_{tot}}{\partial t} = \frac{\partial}{\partial t} \sum_j \sum_i \left[n_{i,j} \bar{H}_{i,j}^{avg} + \int_{v_j} c_{i,j} (\bar{H}_{i,j} - \bar{H}_{i,j}^{avg}) dv_j \right]. \quad (3)$$

The first term on the right side of Equation 3 represents the rate of change

of the enthalpy of the cell if all species are present at their average composition. The second term is a correction accounting for composition variations. In the development that follows, the first term in Equation 3 will be split into three separate terms. Applying the product rule for differentiation and recalling that

$$\left(\frac{\partial \bar{H}_{i,j}^{avg}}{\partial T} \right)_p = \bar{C}_{p,i,j}^{avg}, \quad (4)$$

we obtain

$$\sum_j \sum_i \frac{\partial}{\partial t} (n_{i,j} \bar{H}_{i,j}^{avg}) = \sum_j \sum_i \left[n_{i,j} \bar{C}_{p,i,j}^{avg} \frac{\partial T}{\partial t} + \bar{H}_{i,j}^{avg} \frac{\partial n_{i,j}}{\partial t} \right], \quad (5)$$

for the first term in Equation 3.

It is assumed that there are several simultaneous electrode reactions of the form

$$\sum_i s_{i,l} M_i^{z_i} = n_l e^- \quad (6)$$

occurring within the battery. The reactions are written so that species i is always in a phase type m , having a certain secondary reference state. For example, in a LiCl-KCl molten salt cell, all the electrode reactions are written so that the ionic lithium species is always present in the molten electrolyte phase and any precipitation of LiCl is accounted for separately.

A species balance may be written as

$$\frac{\partial n_{i,m}}{\partial t} = \sum_l \frac{s_{i,l} I_l}{n_i F} - \sum_{j \neq m} \frac{\partial n_{i,j}}{\partial t}. \quad (7)$$

The first term on the right side of Equation 7 represents the amount of i that is produced or consumed by electrode reactions. The partial current, I_l , is positive for a cathodic reaction and negative for an anodic reaction. The second term accounts for phase changes such as the LiCl precipitation men-

tioned above. Integration of Equation 7 yields

$$n_{i,m} = n_{i,m}^p - \sum_{j \neq m} (n_{i,j} - n_{i,j}^p) + \sum_l \frac{s_{i,l}}{n_l F} \int_0^t I_l dt. \quad (8)$$

We may express partial molar enthalpies in the form

$$\bar{H}_{i,m}^{avg} = H_{i,m}^p - R T^2 \frac{\partial}{\partial T} \ln(\alpha_{i,m}^{avg}). \quad (9)$$

The theoretical open-circuit potential for reaction l at the average composition, relative to a reference electrode of a given kind is given by

$$U_{l,avg} = U_l^p - U_{RE}^p + \frac{RT}{n_{RE} F} \sum_i s_{i,RE} \ln(\alpha_i^{RE}) - \frac{RT}{n_l F} \sum_i s_{i,l} \ln(\alpha_{i,m}^{avg}). \quad (10)$$

By utilizing the Gibbs-Helmholtz relation for each reaction, we may write the standard reaction enthalpy in terms of the standard cell potential,

$$\sum_i \frac{s_{i,l}}{n_l F} H_{i,m}^p = T^2 \frac{\partial}{\partial T} \left(\frac{U_l^p}{T} \right). \quad (11)$$

Looking at Equations 5 and 7, we can see that the contribution to the rate of enthalpy change associated with the electrode reactions may be written as

$$\sum_m \sum_i \bar{H}_{i,m}^{avg} \sum_l \frac{s_{i,l}}{n_l F} I_l = \sum_m \sum_l \frac{I_l}{n_l F} \sum_i \bar{H}_{i,m}^{avg} s_{i,l}. \quad (12)$$

Using Equations 9 and 11, we may write this contribution in terms of the electrode reaction potentials.

$$\sum_m \sum_l \frac{I_l}{n_l F} \sum_i \bar{H}_{i,m}^{avg} s_{i,l} = \sum_l I_l \left[T^2 \frac{\partial}{\partial T} \left(\frac{U_l^p}{T} \right) - \frac{R T^2}{n_l F} \sum_i \frac{\partial}{\partial T} \ln(\alpha_{i,m}^{avg})^{s_{i,l}} \right]. \quad (13)$$

Using Equation 10, we may write Equation 13 in terms of the theoretical open-circuit potentials relative to a reference electrode of a given kind as

$$\sum_l I_l \sum_m \sum_i \frac{\bar{H}_{i,m}^{avg} s_{i,l}}{n_l F} = \sum_l I_l \left[T^2 \frac{\partial}{\partial T} \left(\frac{U_{l,avg}}{T} \right) \right]. \quad (14)$$

The quantity multiplying I_l on the right side and the left side of Equation 14 is sometimes termed the enthalpy voltage of reaction l .

Substitution of Equations 7, 8, and 14 into Equation 5 and placing this result into Equation 3 results in the final form for $\frac{\partial H_{tot}}{\partial t}$. Equating this to $q - IV$ (Equation 1) gives the following form for the energy balance equation:

$$q - IV =$$

$$\begin{aligned}
& \sum_i \left[I_i T^2 \frac{\partial \frac{U_{i,avg}}{T}}{\partial T} \right] && \text{reversible effects} \\
& - \sum_j \frac{\partial}{\partial t} \left[\int_{v_j} \sum_i c_{ij} RT^2 \frac{\partial}{\partial T} \ln \left(\frac{\gamma_{ij}}{\gamma_{ij}^{avg}} \right) dv_j \right] && \text{enthalpy-of-mixing effects} \\
& - \sum_{j \neq m} \sum_i \left[\left(\Delta H_{i \rightarrow m}^o - RT^2 \frac{\partial}{\partial T} \ln \frac{\gamma_{i,m}^{avg}}{\gamma_{ij}^{avg}} \right) \frac{dn_{ij}}{dt} \right] && \text{phase-change terms} \\
& + \frac{\partial T}{\partial t} \left[\sum_j \sum_i n_{ij}^o \bar{C}_{p_{ij}}^{avg} + \sum_i \frac{\int_0^t I_i dt}{n_i F} \Delta C_{p_i} \right] && \text{heat-capacity effects} \\
& + \sum_{j \neq m} \sum_i \left(\bar{C}_{p_{ij}}^{avg} - \bar{C}_{p_{i,m}}^{avg} \right) (n_{ij} - n_{ij}^o) \quad (15)
\end{aligned}$$

where

$$\Delta C_{p_i} \equiv \sum_i s_{i,l} \bar{C}_{p_{i,m}}^{avg} \quad (16)$$

and

$$\Delta H_{i \rightarrow m}^o \equiv H_{i,m}^o - H_{ij}^o \quad (17)$$

It should be recognized that all the composition dependence of Equation 15 may be expressed in terms of activity coefficients. This is a reflection of the fact that the composition dependence of any thermodynamic quantity is completely determined if the activity coefficient behavior of the species is known. This analysis does not include enthalpy changes associated with non-faradaic reactions. Also, the heat capacities of the battery support materials should be understood to be included in Equation 15. Actually, in most practi-

cal applications the heat capacity of a battery module does not change substantially during operation. In such cases, the heat capacity term in Equation 15 may be replaced by some average value. Also, the rate of heat transfer q between the battery and surroundings may be expressed as

$$q = -hA(T - T_A) \quad (18)$$

where the heat-transfer coefficient h is based on separator area and is estimated from the heat losses for a battery module.

As an example of how Equation 15 may be used, let us apply it to the LiAl/LiCl-KCl/FeS battery. We shall assume that any number of reactions may be occurring and that all the reacting phases are pure except the electrolyte. The molten LiCl-KCl electrolyte phase is considered to be a solution of varying composition throughout the battery. The species present are the Li^+ , K^+ and Cl^- in the electrolyte and those corresponding to the pure reacting phases. The open-circuit potential data are considered to be given at the eutectic composition of the electrolyte as a reference condition and to be of the form $U_{i,out} = a_i + b_i T$. All the electrode reaction potentials are given relative to the two phase LiAl alloy reference electrode. We may relate $U_{i,out}$ to $U_{i,avg}$ by

$$U_{i,avg} = U_{i,out} - \frac{RT}{F} \ln \left[\left[\frac{a_{LiCl}^{avg}}{a_{LiCl}^{out}} \right]^{\frac{s_{Li^+,i}}{n_i}} \left[\frac{a_{LiCl}^{avg}}{a_{LiCl}^{out}} \right]^{\frac{-s_{Li^+,RE}}{n_{RE}}} \left[\frac{a_{KCl}^{avg}}{a_{KCl}^{out}} \right]^{\frac{s_{K^+,i}}{n_i}} \right] \quad (19)$$

The resulting equation will allow for precipitation of pure LiCl and pure KCl solid phases. With the above considerations, Equation 15 becomes

$$MC_p^m \frac{\partial T}{\partial t} = -hA(T - T_A) - IV \quad (20)$$

$$+ \sum_i I_i \left[a_i + \frac{RT^2}{F} \frac{\partial}{\partial T} \ln \left[\left(\frac{\gamma_{LiCl}^{avg}}{\gamma_{LiCl}^{ref}} \right)^{s_{Li+Li}} \left(\frac{\gamma_{LiCl}^{avg}}{\gamma_{LiCl}^{ref}} \right)^{-s_{Li+RE}} \left(\frac{\gamma_{KCl}^{avg}}{\gamma_{KCl}^{ref}} \right)^{s_{K+Li}} \right] \right]$$

$$+ \frac{\partial}{\partial t} \int_v \varepsilon RT^2 \left[c_{LiCl} \frac{\partial}{\partial T} \ln \left(\frac{\gamma_{LiCl}}{\gamma_{LiCl}^{avg}} \right) + c_{KCl} \frac{\partial}{\partial T} \ln \left(\frac{\gamma_{KCl}}{\gamma_{KCl}^{avg}} \right) \right] dv$$

$$- \frac{dn_{LiCl_s}}{dt} \left[\Delta H_{LiCl_s}^0 + RT^2 \frac{\partial \ln \gamma_{LiCl}^{avg}}{\partial T} \right] - \frac{dn_{KCl_s}}{dt} \left[\Delta H_{KCl_s}^0 + RT^2 \frac{\partial \ln \gamma_{KCl}^{avg}}{\partial T} \right]$$

where $\frac{dn_{LiCl_s}}{dt}$ and $\frac{dn_{KCl_s}}{dt}$ are the crystallization rates of solid $LiCl$ and KCl phases, respectively. There is a considerable amount of simplification involved in going from Equation 15 to Equation 20. For example, the ionic activity coefficients, ionic concentrations, and ionic partial molar enthalpies have been combined into neutral combinations that refer to undissociated $LiCl$ and KCl . If the electrolytes were considered to be completely dissociated, then Equation 15 could be rearranged to contain mean ionic activity coefficients (neutral combinations of individual ionic activity coefficients).

In the next section each of the terms in Equation 15 will be discussed. In the following section Equation 20 will be applied, more specifically, to the $LiAl/FeS$ cell.

Discussion of Terms

Reversible Effects

During discharge, the chemical energy of the cell is directly converted into work in the form of electricity. The energy that the cell delivers is a maximum when the cell operates reversibly. This maximum, expressed as a rate, may be written as

$$IV_{rev} = \sum_i I_i \left[U_{i,avg} \right], \quad (21)$$

and is tucked into the reversible effects term in Equation 15. The difference between V_{rev} and V is the cell overpotential. The overpotential is indicative of irreversibilities such as ohmic losses, charge-transfer overpotentials, and mass-transfer limitations.

Also housed in this reversible effects term is the reversible heat generation,

$$q_{rev} = - \sum_i I_i \left[T \frac{\partial (U_{i,avg})}{\partial T} \right]. \quad (22)$$

If we do not consider enthalpy-of-mixing and phase-change terms in Equation 15, then Equations 21 and 22 represent the power and the heat generation that accompany reversible isothermal cell operation, respectively. The reversible work is related to the change in Gibbs function of the cell's contents. The reversible heat is related to the entropy change. We may write Equation 15 in terms of the reversible heat and work contributions as

$$q = IV - \sum_i I_i \left[U_{i,avg} - T \frac{\partial U_{i,avg}}{\partial T} \right] + MC_p^m \frac{\partial T}{\partial t} \quad (23)$$

(without considering enthalpy-of-mixing and phase-change terms). This equation is the form of the energy balance that is most commonly encountered in the literature. The composition dependence of the open-circuit

potential is housed in $U_{i,avg}$ (see Equation 10). Of course, combining the q_{rev} and IV_{rev} terms and rearranging will give the reversible effects term in Equation 15. Thus, we may combine these terms and write Equation 23 as

$$q = IV + \sum_i I_i \left[T^2 \frac{\partial}{\partial T} \frac{U_{i,avg}}{T} \right] + MC_p^m \frac{\partial T}{\partial t} \quad (24)$$

This combination has the advantage that a strong composition dependence of the two terms separately may partially cancel in the enthalpy voltage.

If the open-circuit potentials $U_{i,avg}$ are independent of composition and linearly related to temperature, then the reversible effects term in Equation 15 becomes

$$\text{reversible effects} = -\sum_i I_i a_i \quad (25)$$

Notice that the temperature coefficients, b_i , are not needed.

Enthalpy-of-Mixing Effects

The enthalpy-of-mixing term represents the heat effects associated with generation or relaxation of concentration profiles. For example, if we do not consider phase-change terms, then this term represents the rate of heat generation after current interruption of cell operation. First, the definition of the average composition will be discussed. Later, an estimate of the adiabatic temperature rise due to relaxation of concentration profiles in a lead-acid cell after full discharge will be made.

The enthalpy-of-mixing term is the only term in Equation 15 that is dependent on the spatial variation of composition. This term may be thought of as a correction because the other terms depend only on the average composition. The term is difficult to treat because it involves integrations of concentration profiles. Consequently, it is instructive to discuss the conditions under which it may be neglected. The definition of the average composition of species i is arbitrary. Therefore, if mixing effects are to be neglected then the average composition should be chosen such that the value of this neglected term is minimized. For a binary phase it can be shown that the integral in the mixing term may be minimized if the average concentration is defined as

$$c_i^{avg} = \frac{\int_v c_i dv}{\int_v dv} \quad \text{or} \quad x_i^{avg} = \frac{\int_v c x_i dv}{\int_v c dv}, \quad (26)$$

where

$$c = c_1 + c_2.$$

This will be shown as follows. For a binary system, the integral in the mixing term in Equation 15 may be written as

$$\int_v c [H - (x_1 \bar{H}_1^{avg} + x_2 \bar{H}_2^{avg})] dv . \quad (27)$$

where the molar enthalpy is defined as

$$H = x_1 \bar{H}_1 + x_2 \bar{H}_2 ,$$

and \bar{H}_i^{avg} is the partial molar enthalpy of species i at the average composition. It should be recognized that in this development it is assumed that the spatial variation of composition is fixed and that Equation 27 is only a function of x_1^{avg} . By writing the mixing integral in this form, we may obtain a clearer interpretation of the mixing term. The sum subtracted from H is the tangent line to the enthalpy-vs-composition ($H - x_1$) plot at the average composition. The integral may be considered to be a measure of the ability to approximate the H curve with a tangent, in the range of composition variation throughout the cell. Therefore, if the enthalpy curve is linear in this range, then \bar{H}_1 and \bar{H}_2 are independent of composition, and the integral is zero regardless of the value of x_1^{avg} . Also, if the activity coefficients are independent of temperature (see Equation 9) then mixing effects can be ignored. Different choices of the tangent, corresponding to different values of the average composition may give better or worse approximations of the enthalpy curve. Equation 27 may be minimized with respect to the average composition by solving the following equation for x_1^{avg} :

$$\frac{d}{dx_1^{avg}} \left[\int_v c (x_1 \bar{H}_1^{avg} + x_2 \bar{H}_2^{avg}) dv \right] = 0 . \quad (28)$$

In formulating Equation 28, it was recognized that the composition profiles and enthalpy curve are independent of the choice of x_1^{avg} . We may further simplify Equation 28 and write

$$\int_{\nu} c_1 d\nu \frac{d\bar{H}_1^{avg}}{dx_1^{avg}} + \int_{\nu} c_2 d\nu \frac{d\bar{H}_2^{avg}}{dx_1^{avg}} = 0. \quad (29)$$

The Gibbs-Duhem equation,

$$x_1^{avg} \frac{d\bar{H}_1^{avg}}{dx_1^{avg}} + x_2^{avg} \frac{d\bar{H}_2^{avg}}{dx_1^{avg}} = 0. \quad (30)$$

may be applied, and Equation 29 may be solved for x_1^{avg} as given in Equation 26. The corresponding development for multicomponent mixtures is given in Appendix A. Equation 26 is guaranteed to be the choice of the average composition that will minimize Equation 27 only if the integral has simple behavior. The behavior is said to be simple if the second derivative of the integral is non-zero for all possible values of x_1^{avg} (in range of concentration variation throughout the cell). For example, if the integral has a point of inflection such that its value may be either positive or negative depending upon x_1^{avg} , then x_1^{avg} may be chosen so that the integral is zero. In this case, the best choice of the x_1^{avg} is not necessarily defined by Equation 26. Regardless of the behavior of the integral, Equation 26 is the most convenient definition of the average composition. It has physical significance, and it is usually a simple function of state-of-charge. It is the final uniform composition of a concentration profile that is allowed to relax, and the energy effect associated with this process, in this case, is proportional to the value of the integral for the initial profile.

It is useful to examine further the sign of the integral. The sign of Equation 27 will indicate such things as whether mixing effects will tend to heat up, or cool down, a cell during operation. It is convenient now to look at Equation 27 as a function of the mixing behavior and assume that that average composition is fixed. Equation 27 will be positive if

$$H > (x_1 \bar{H}_1^{avg} + x_2 \bar{H}_2^{avg}). \quad (31)$$

The right side of Equation 31 is linear in x_1 . If Equation 31 is differentiated twice with respect to x_1 , we obtain

$$\frac{d^2 H}{dx_1^2} > 0. \quad (32)$$

In other words, in the range of concentration variation throughout the cell, if the enthalpy curve is always concave upward then the integral will be positive. Conversely, the integral will be negative if the enthalpy curve is everywhere concave downward. For example, in the lead-acid cell, the sulfuric acid-water system has an enthalpy curve that is always concave upward. Consequently, the temperature of a well-insulated lead-acid cell will always increase after current interruption during operation due to relaxation of concentration profiles. To illustrate this, in Appendix A Equation 15 is used to estimate this temperature rise. The temperature rise, after full discharge, is approximately 1.8 K. It is also important to investigate the consequence of neglecting mixing effects in thermal calculations. For the lead-acid cell, the temperature during operation (generation of concentration profiles) is overestimated if calculations are made by neglecting the mixing term. The situation is reversed for a high temperature cell employing LiCl-KCl electrolyte. In the range of concentration variation throughout this cell the enthalpy curve is always concave downward and the cell temperature will decrease due to mixing effects after current interruption. Calculations that neglect mixing will give underestimations of temperature when concentration profiles are being generated (during cell operation). This will be investigated in greater detail later.

If the enthalpy curve, in the range of composition variation, may be concave upward or concave downward, then the sign of the integral depends on the choice of the average composition. Certain associated systems, such

as ethanol and water, exhibit inflection points in their enthalpy curves.

Phase-Change Terms

In the reversible effects term of Equation 15, all the reactions have species i in the same phase type m . For example, in Equation 20 LiCl is always present as a molten LiCl-KCl solution phase in all reactions. However, one of the phases present in the cell during operation may be pure solid LiCl. The purpose of the phase-change terms is to account for the enthalpy change due to crystallization of this solid phase. For example, ice crystals form during low temperature operation of aqueous batteries and a energy balance such as Equation 23 would not correctly predict cell temperatures. If the m phase types in the reversible effects contribution (Equation 15) are the only phases present in the cell during operation, then the phase-change terms are zero.

Heat-Capacity Effects

The quantities to the right of $\frac{\partial T}{\partial t}$ in the heat-capacity effects term of Equation 15 represent the heat capacity of the cell. This heat capacity changes with time because the composition of the cell changes due to electrochemical reactions and phase changes. The first part of this heat capacity represents the initial heat capacity of the cell's reactive material. The heat capacity of the cell's inert supporting material should be included in this part. The second and third parts account for changes in the initial heat capacity as a result of electrochemical reactions and phase changes, respectively.

As mentioned earlier, the total heat capacity of a typical cell (including supporting material) is approximately constant so that this term usually reduces to a simple expression.

Description of Examples

The results of applying Equation 15 to the existing model of the LiAl/LiCl,KCl/FeS cell will be given. The purpose of these examples is to illustrate how the energy balance equation may be applied to a specific system and to examine the relative contributions corresponding to the terms in this equation. The use of Equation 15 is best illustrated by application to a mathematical model of a battery in which concentration profiles can be used to calculate energy contributions from mixing, and current fractions can be used to calculate energy contributions from simultaneous reactions. This model was originally developed by Pollard and Newman in 1981, and the details of the theoretical analysis are given in their publications.^[9,10] The model gives the galvanostatic discharge behavior of a one-dimensional cell sandwich consisting of a porous LiAl negative electrode, porous FeS positive electrode, electrolyte reservoir, and separator. The model simulates the discharge processes in the positive as the two simultaneously occurring reactions given as mechanism 1 in Table 1. Pawlikowski^[13] in 1982 developed a model of the cell with mechanism 2 as the positive electrode discharge reactions. Mechanisms 1 and 2 yield the same overall reaction and differ mainly in the intermediate phase (X-phase or J-phase).

The electrochemistry of the FeS electrode is reasonably well understood. The actual discharge processes are complicated and are more like a mixture of the two proposed mechanisms along with simultaneously occurring chemical reactions. There is evidence, however, for the simple 2-reaction mechanisms under certain operating conditions.^[11] In practice, batteries are operated between 400°C and 500°C. Higher operating temperatures and LiCl concentrations tend to favor mechanism 1. Lower temperatures and LiCl concentrations favor mechanism 2. Discharge through the X-phase intermediate is preferred because of the poor reversibility of the J-

Table 1.
Model discharge mechanisms in the FeS electrode

Reaction	α_i^* [V]	$b_i * 10^3$ [V/K]
Mechanism 1 (X-phase intermediate)		
1) $\text{FeS} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{FeS}_2$ (X-phase)	1.367	-0.022
2) $\text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 2\text{Li}_2\text{S} + \text{Fe}$	1.454	-0.178
Mechanism 2 (J-phase intermediate)		
3) $26\text{FeS} + \text{Li}^+ + \text{Cl}^- + 6\text{e}^- \rightarrow \text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl} + 2\text{Fe}$ (J-phase)	1.955	-0.680
4) $\text{J} + 51\text{Li}^+ + 46\text{e}^- \rightarrow 26\text{Li}_2\text{S} + 24\text{Fe} + 6\text{K}^+ + \text{Cl}^-$	1.440	-0.024

* α_i and b_i were obtained from Reference 11.

phase reactions. For purposes of comparison, the simulations of the two mechanisms will use the same initial temperature and electrolyte composition.

The model discharges are meant to simulate a well insulated (but not adiabatic) battery operating in an ambient temperature environment with no external heating. The relevant input data and energy equation specific to each mechanism are given in Appendix B.

Results

Figure 1 gives the cell temperature as a function of state of charge for both mechanisms. The dashed lines show the temperature profile for adiabatic and reversible discharge. Under these conditions the two mechanisms yield the same temperature at 100% depth of discharge because the overall reaction is the same. In both cases the reactions are exothermic, so that the cell temperature increases throughout discharge. Though the adiabatic/reversible profile of mechanism 1 appears linear, there is actually a slight amount of curvature due to the logarithmic dependence of the cell temperature. The composition dependencies associated with the J-phase reactions result in the more discernible curvature of each portion of the adiabatic/reversible profile of mechanism 2. The criterion of reversibility allows the stoichiometry of the reactions to yield the discontinuities in slope located at 50% and 12% for mechanism 1 and mechanism 2, respectively. For example, with mechanism 1 up to 50% utilization only reaction 1 occurs, and after this point reaction 2 occurs. The dashed curve in Figure 2 is the heat generation rate for reaction 1. It is approximately constant because the temperature is not changing substantially, and this is responsible for the apparent linearity in Figure 1. With the J-phase reactions, the stoichiometry dictates the transition from reaction 3 to reaction 4 to occur at 12% utilization.

It is interesting to compare these results to the results of the more realistic simulations. The solid lines in Figure 1 are the results of the mathematical models. The relevant input data and energy equation specific to each mechanism are given in Appendix B. In these simulations, the irreversibilities associated with ohmic losses, migration effects, mass-transfer, and charge-transfer overpotentials cause electrode polarization. The onset of the second reaction of each mechanism may occur before the

prediction based on reversibility because of the resulting potential distribution in the porous, positive electrode. Compared to the values of 50% and 12% utilization, the second reaction begins at 30% and 11% utilization for mechanisms 1 and 2, respectively. At these operating conditions, the reaction potential difference $U_{3,avg} - U_{4,avg}$ for the J-phase mechanism is always about four times larger than the difference $U_{1,avg} - U_{2,avg}$ for the X-phase mechanism; we see that the onset of the second reaction occurs closer to the reversible prediction in the case of the J-phase mechanism because a larger positive electrode polarization is required to promote the onset of the second reaction as compared with the X-phase mechanism.

The solid lines in Figure 2 are plots of the terms in Equation B-1 as functions of state of charge for the X-phase mechanism up to 30% utilization. The dashed line in Figure 2 is called the entropic-heat and has the value of $-i_1 b_1 T$. It would be the only term on the right side of Equation B-1 if the equation was written for the adiabatic/reversible case. The polarization-heat, $i_1(U_{1,avg} - V)$, and the entropic-heat add up to the enthalpy-of-reaction and electrical-work term. The heat-loss contribution does not change markedly because the cell is well insulated, and the overall cell temperature does not change substantially. The profile for the X-phase mechanism in Figure 1 follows the adiabatic/reversible profile up to about 5% utilization because the heat-loss contribution tends to cancel the polarization-heat. The polarization-heat is mainly responsible for the increasing departure of the cell temperature from the reversible case throughout discharge. With increasing utilization, the polarization-heat increases because the open-circuit potential ($U_{1,avg}$) is approximately constant and the cell voltage drops.

These results can be contrasted to the results with the J-phase mechanism from 0% to 11% utilization. The average LiCl concentration increases,

and the composition dependent $U_{3,avg}$ decreases accordingly (Equation 19). Actually, $U_{3,avg}$ decreases at about the same rate as the cell voltage, so that the polarization-heat remains relatively constant. Up to about 5% utilization, the heat-loss term approximately cancels the polarization-heat, and the temperature profile follows the adiabatic/reversible case. The cell temperature increases enough from 5% to 11% utilization so that the heat-loss term dominates, and the temperature remains below the adiabatic/reversible case. After 12% utilization the heat losses and $U_{4,avg}$ stay approximately constant, so that the polarization-heat dominates, and by 36% utilization the profile lies above the adiabatic/reversible case.

Although the mixing term offers a negligible contribution to the energy balance, it is interesting to investigate the processes that determine its behavior. As we mentioned earlier, for the molten LiCl-KCl system, the value of the integral in Equation B-1 is always negative. Therefore, if the heat losses are made negligible, the cell temperature will decrease after current interruption. Prior to the onset of precipitation, this is entirely a mixing effect. At 25% utilization in Figure 2, this temperature decline is only about 0.2 K. Before precipitation, the concentration of LiCl steadily decreases in the positive electrode and increases in the negative electrode, and the average composition, $x_{LiCl}^{avg} = 0.58$ (defined by Equation 26), is constant. The mixing term (the time derivative of the integral) also increases, and the cell temperature would be slightly underestimated if mixing effects were ignored. The concentration throughout the separator and reservoir volumes remains close to the average composition, so that their contributions to the integral are two orders of magnitude smaller than the contributions from integration through the electrodes. Figure 2 shows that the integral increases in magnitude to the point where the mixing term is zero (26.5% utilization). After this point the mixing term is slightly negative

corresponding to a decrease in the magnitude of the integral with time. The mixing term decreases when KCl precipitates because in the region of precipitation the electrolyte composition is approximately constant at its saturation value. Following the onset of precipitation, the adiabatic temperature decline after current interruption is determined by the more complex processes of simultaneous melting of KCl and electrolyte mixing. We present the breakdown of contributions only up to 30% utilization because when the second reaction begins simultaneously, reaction heat effects and precipitation effects cause oscillatory behavior. The description and discussion of this phenomenon will be treated in a subsequent publication.

Conclusions

The examples presented help to illustrate that the processes involved in cell heat generation may be complex and that the application of a sufficiently general energy equation is advantageous. Equation 23, written for a single cell reaction, is the energy equation most commonly used in battery applications. The use of this form of a energy balance is justified only if phase-change effects, mixing effects, and simultaneous reactions are not important. An energy equation including the effects mentioned above is of course most easily applied to modeling studies. However, applying an energy equation that includes the effects of simultaneous reactions to experimental measurements may help elucidate reaction mechanisms. For example, if heat generation rates and cell voltage measurements are made on LiAl/FeS cells under isothermal operating conditions, an energy equation may be fit to the experimental data to determine the current fractions of simultaneously occurring reactions. The experiments performed under truly isothermal conditions have the advantage that an estimate of the mean cell heat capacity is not required. However, if experimental cells are not maintained isothermal, then heat capacity effects or the effects of non-uniform temperature may obscure the relationship of the experimental results to the energy balance.

A reversible/isothermal model is relatively easy to construct from knowledge of the stoichiometry of the probable cell reactions and the temperature dependence of their open-circuit potentials. The comparison of such a model with experimental results may also aid in the understanding of the system, just as the adiabatic/reversible model was used to aid in the interpretation of the simulation of the well-insulated cell in the examples. Regardless of the application, understanding the fundamental processes involved in cell heat generation will aid in our ability to design and develop

more efficient and reliable battery systems.

Appendix A

Choice of the Average Composition for a Multicomponent System

For a multicomponent phase, the integral in Equation 15 may be written as

$$\int_V \sum_i c_i x_i (\bar{H}_i - \bar{H}_i^{avg}) dv . \quad (A-1)$$

In this development it will be assumed that Equation A-1 is only a function of the average composition and that the spatial variation of composition is fixed. If the molar enthalpy is defined as

$$H = \sum_i x_i \bar{H}_i . \quad (A-2)$$

Equation A-1 may be written as

$$\int_V c [H - \sum_i x_i \bar{H}_i^{avg}] dv . \quad (A-3)$$

In certain cases, Equation A-1 is minimized with respect to the average composition by equating the total differential to zero. Recognizing that the enthalpy is independent of the choice of the average composition we may write

$$d \left[\sum_i \int_V \bar{H}_i^{avg} c_i x_i dv \right] = \sum_i \left(\int_V c_i x_i dv \right) d\bar{H}_i^{avg} = 0 . \quad (A-4)$$

If we multiply and divide each term in Equation A-4 by x_i^{avg} ,

$$\sum_i \left(\frac{\int_v c x_i dv}{x_i^{avg}} \right) x_i^{avg} d\bar{H}_i^{avg} = 0, \quad (\text{A-5})$$

and compare this to the Gibbs-Duhem equation,

$$\sum_i x_i^{avg} d\bar{H}_i^{avg} = 0, \quad (\text{A-6})$$

we see that the bracketed quantity in Equation A-5 must be equal to a constant. This constant,

$$K = \frac{\int_v c x_i dv}{x_i^{avg}} \quad (\text{A-7})$$

must be independent of x_i^{avg} in order to satisfy the Gibbs-Duhem equation. If we apply a mole fraction balance,

$$\sum_i x_{i,avg} = \frac{\sum_i \int_v c x_i dv}{K} = 1, \quad (\text{A-8})$$

we may solve for this constant,

$$K = \int_v c dv. \quad (\text{A-9})$$

Substituting this into Equation A-7, we obtain the final form for the average composition,

$$x_i^{avg} = \frac{\int_v c x_i dv}{\int_v c dv}. \quad (\text{A-10})$$

Equation A-10 is guaranteed to be the average composition that minimizes Equation A-1 only if its second total differential is positive for all possible values of x_i^{avg} .

Estimate of the Temperature rise in a Lead-Acid Cell
Following Current Interruption

Prior to discharge, the cell is assumed to have a uniform composition of 5 molal sulfuric acid. It is assumed that one-third of the electrolyte is contained in the cathode and anode spaces, and one-third is in the space between the electrodes. It is also assumed that during discharge the concentration of acid in the intermediate space remains unchanged and that the acid concentrations throughout the electrode compartments are uniform. Basing the discharge on two Faradays and a transference number of 0.74 for hydrogen ion, we may calculate the concentration in the cathode space and anode space to drop to 1.04 and 2.79 molal, respectively¹⁴. If we regard the cell as well insulated and there are no phase changes (such as formation of ice crystals), Equation 15 may be written as

$$1.15 \frac{\partial T}{\partial t} (n_{PbSO_4} C_{PbSO_4} + n_1 \bar{C}_{P_1}^{avg} + n_2 \bar{C}_{P_2}^{avg}) = \quad (A-11)$$

$$- \frac{\partial}{\partial t} \int_V c [H - (x_1 \bar{H}_1^{avg} + x_2 \bar{H}_2^{avg})] dv.$$

In writing this Equation, it is assumed that the heat capacity of the battery support material is 15% of the heat capacity of the reactive material. The integral on the right side is easy to evaluate in this case because the concentration is uniform and the volume is the same in each compartment. The average composition of acid, defined by Equation 26, is 2.95 molal. As mentioned earlier, this is the final uniform concentration after relaxation, and the temperature rise is proportional to the value of the integral for the initial profile. Using the data available in Reference 14 (for 298 K), we may calculate the temperature rise to be about 1.8 K. We recognize that the

assumed concentration jumps at the interfaces are artificial and that, realistically, diffusion tends to equalize the concentrations. The estimated temperature rise would be slightly lower if the above effect were taken into account. We must also, however, recognize the effects of non-uniform reaction distribution in porous electrodes and that this will tend to make the concentration distribution non-uniform. Reference 8 gives spatial distributions of concentration and reaction for a one-dimensional model of a lead-acid cell.

Appendix B

Energy Equations for Model Studies

Mechanism 1 (The number subscripts refer to the reactions in Table 1)

$$\frac{M}{A} C_p^m \frac{\partial T}{\partial t} = \quad (B-1)$$

$$\begin{aligned} & -h(T - T_A) && \text{heat losses} \\ & + (i_1 a_1 + i_2 a_2) - V(i_1 + i_2) && \text{enthalpy of reaction} \\ & && \text{and electrical work} \\ & + \frac{\partial}{\partial t} \int_0^L \epsilon R \left[c_{LiA} T \ln \left(\frac{\gamma_{LiA}}{\gamma_{LiA}^{ref}} \right) + c_{KCl} T \ln \left(\frac{\gamma_{KCl}}{\gamma_{KCl}^{ref}} \right) \right] dy && \text{mixing} \\ & + \frac{1}{A} \frac{dn_{KCl_2}}{dt} \left[\Delta H_{KCl_2}^0 + R T \ln \gamma_{KCl_2} \right] && \text{KCl precipitation} \end{aligned}$$

Mechanism 2

The energy equation for mechanism 2 differs only in the enthalpy-of-reaction and electrical-work term which may be written as

$$\begin{aligned} & + (i_3 a_3 + i_4 a_4) - V(i_3 + i_4) && (B-2) \\ & - i_3 \frac{RT}{F} \ln \left[\left(\frac{\gamma_{LiA}}{\gamma_{LiA}^{ref}} \right)^{5/8} \left(\frac{\gamma_{KCl}}{\gamma_{KCl}^{ref}} \right)^{-1} \right] - i_4 \frac{RT}{F} \ln \left[\left(\frac{\gamma_{LiA}}{\gamma_{LiA}^{ref}} \right)^{-5/48} \left(\frac{\gamma_{KCl}}{\gamma_{KCl}^{ref}} \right)^{-3/23} \right] \end{aligned}$$

Relevant Input Data

quantity	value	quantity	value
x_{Li}^0	0.58(eutectic)	MC_p^m / A	1.89 J/cm ² -K
H_{Ka}^0	26530. J/mol	i	0.0416 A/cm ²
h	$8.25 \cdot 10^{-6}$ W/cm ² -K	T_A	273.15 K
capacity	835.27 C/cm ²	$\epsilon_{\beta S}$	0.555

$$\ln \gamma_{Li} = 723.15 (0.52628x_{Ka} - 1.2738x_{Ka}^2 - 2.9783x_{Ka}^3)$$

$$\ln \gamma_{Ka} = 723.15 (-0.52628x_{Li} - 5.7413x_{Li}^2 + 2.9783x_{Li}^3 - 0.52628 \ln x_{Ka})$$

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List of Symbols

$a_{i,j}$	activity of species i in phase j
a_i^{RE}	activity of species i in the reference electrode
A	separator area, cm^2
a_l	constant in the expression for the open circuit potential of reaction l , V
b_l	temperature coefficient in the expression for the open circuit potential of reaction l , V/K
$c_{i,j}$	concentration of species i in phase j , mol/cm^3
C_p^m	mean heat capacity at constant pressure, J/g-K
$\bar{C}_{p,i,j}$	partial molar constant pressure heat capacity of species i in phase j , J/mol-K
dv_j	differential volume element of phase j , cm^3
e^-	symbol for an electron
F	Faraday's constant, 96,487 C/equiv
h	heat transfer coefficient, $\text{W}/\text{cm}^2\text{-K}$
H_{tot}	enthalpy, J
H	molar enthalpy, J/mol
$H_{i,m}^{\circ}$	molar enthalpy of species i in the secondary reference state corresponding to phase type m , J/mol
$\bar{H}_{i,j}$	partial molar enthalpy of species i in phase j , J/mol
i_l	partial current density of electrode reaction l , A/cm^2
I	cell current, A
I_l	partial current of electrode reaction l , A
K	constant in Equation A-7, mol
L	length of electrode, cm
M	mass of the cell, g
M_i	symbol for the chemical formula of species i

n_l	number of electrons involved in reaction l
n_{RE}	number of electrons involved in the reference electrode reaction
$n_{i,j}$	moles of species i in phase j , moles
q	heat transfer rate, W
R	universal gas constant, 8.3143 J/mol-K
$s_{i,l}$	stoichiometric coefficient of species i in reaction l
t	time, s
T	absolute temperature, K
$U_{l,avg}$	theoretical open-circuit potential for reaction l at the average composition relative to a reference electrode of a given kind, V
U_l°	standard electrode potential for reaction l , V
U_{RE}°	standard electrode potential for the reference electrode reaction, V
v_j	see dv_j
V	cell potential at terminals, V
$x_{i,j}$	mole fraction of species i in phase j
y	distance from electrode, cm
z_i	charge number of species i

Greek

ε	porosity
$\gamma_{i,j}$	activity coefficient of species i in phase j

Subscripts

A	ambient
f	heat of fusion
i	refers to a species
j, m	refer to phases
l	refers to a reaction
rev	reversible

tot total

Superscripts

avg average

eut eutectic composition

m mean

o refers to standard reference state or initial

RE reference electrode

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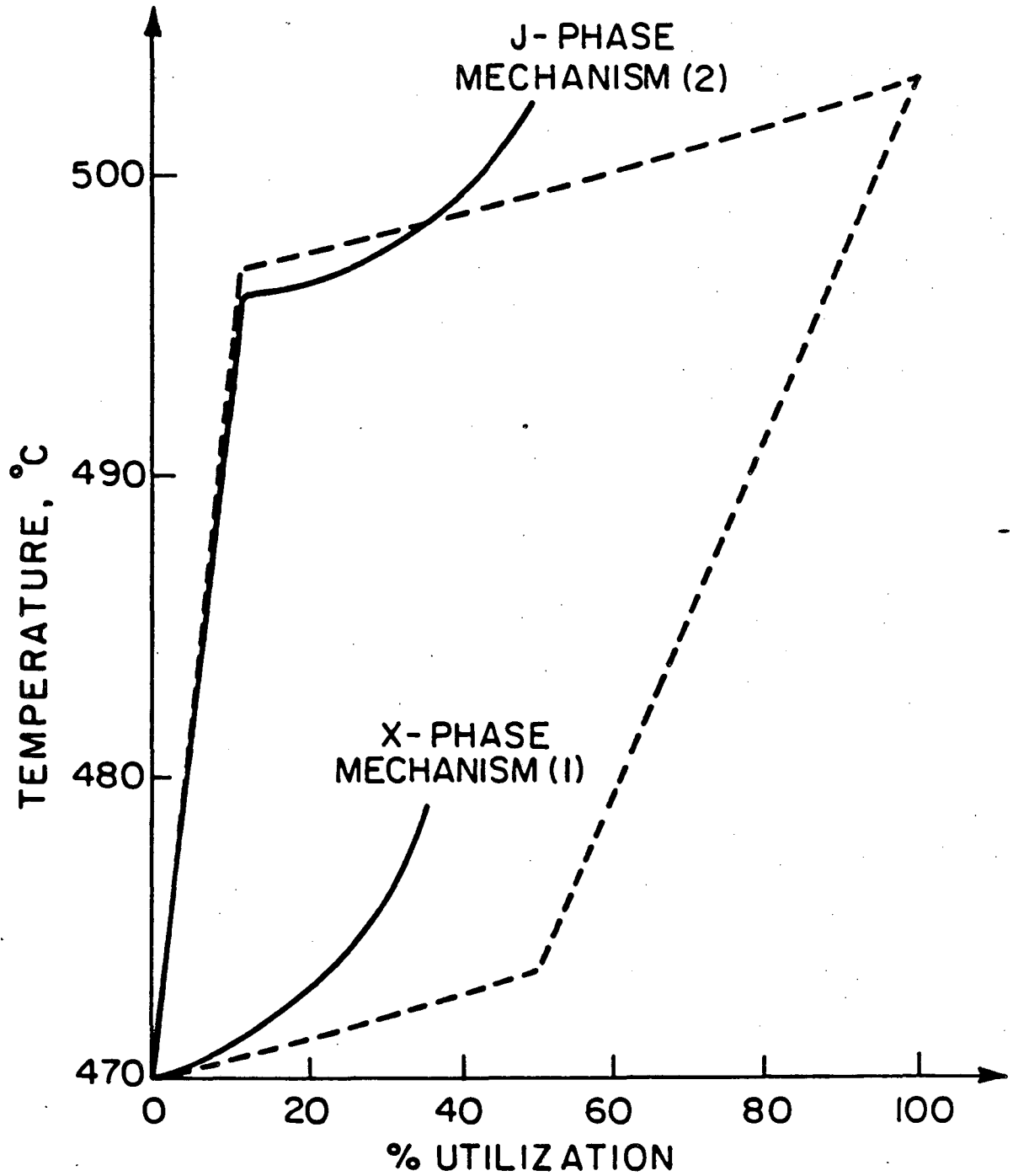
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Figure Captions

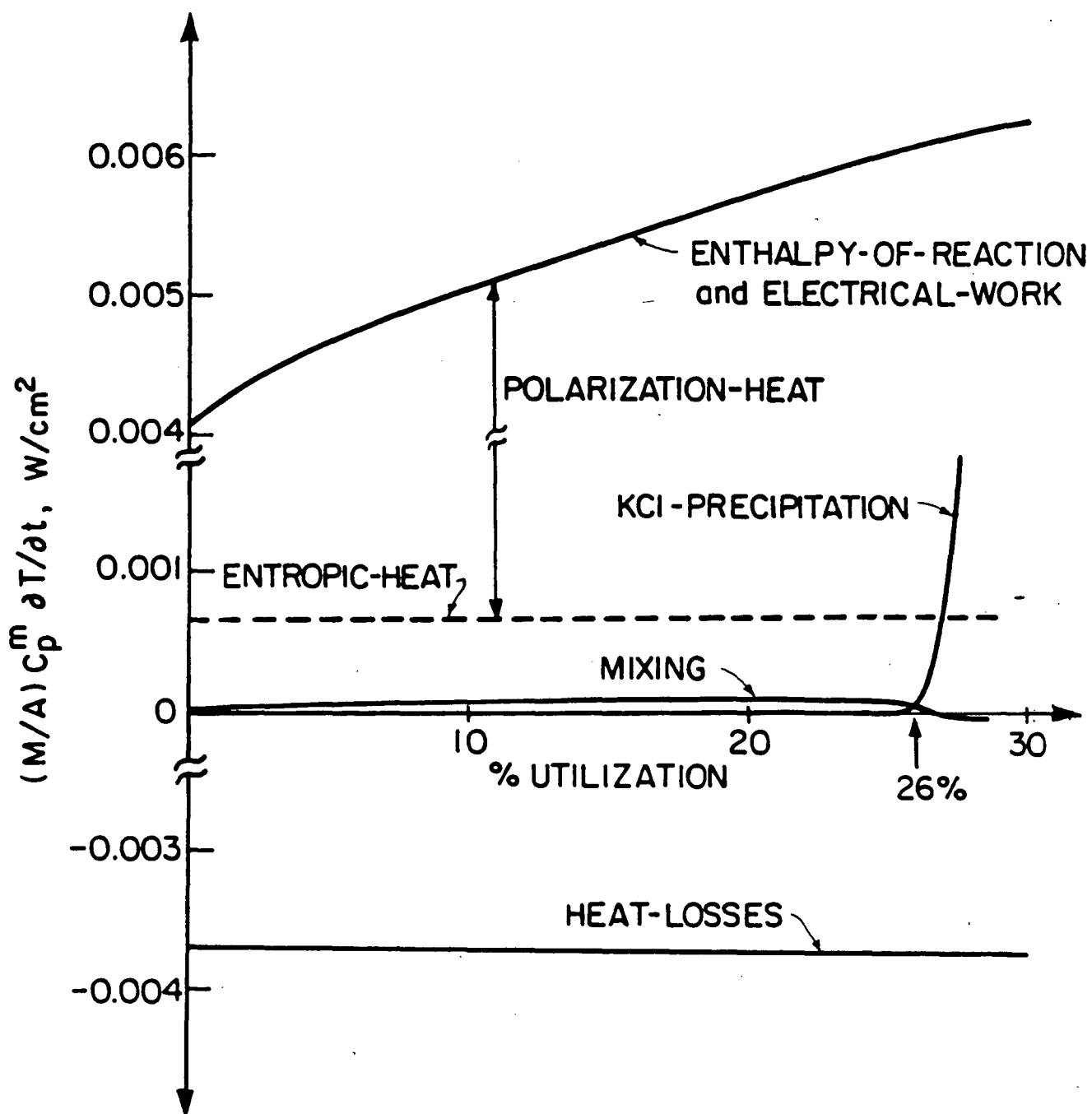
1. Cell temperature as a function of state of charge for mechanism 1 and mechanism 2. The dashed lines are for adiabatic/reversible discharge. The solid lines are the results of the mathematical model simulations. KCl precipitation starts at 26% utilization for the X-phase mechanism and at 42% utilization for the J-phase mechanism. The second reaction starts at 30% utilization for the X-phase mechanism and at 11% utilization for the J-phase mechanism. Cutoff voltages of 1.2 and 1.0 volts were used for mechanisms 1 and 2, respectively.

2. Contributions to the temperature rise in a LiAl/FeS cell (corresponding to the terms in Equation B-1).



XBL844-6939

Figure 1



XBL 844-6940

Figure 2

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