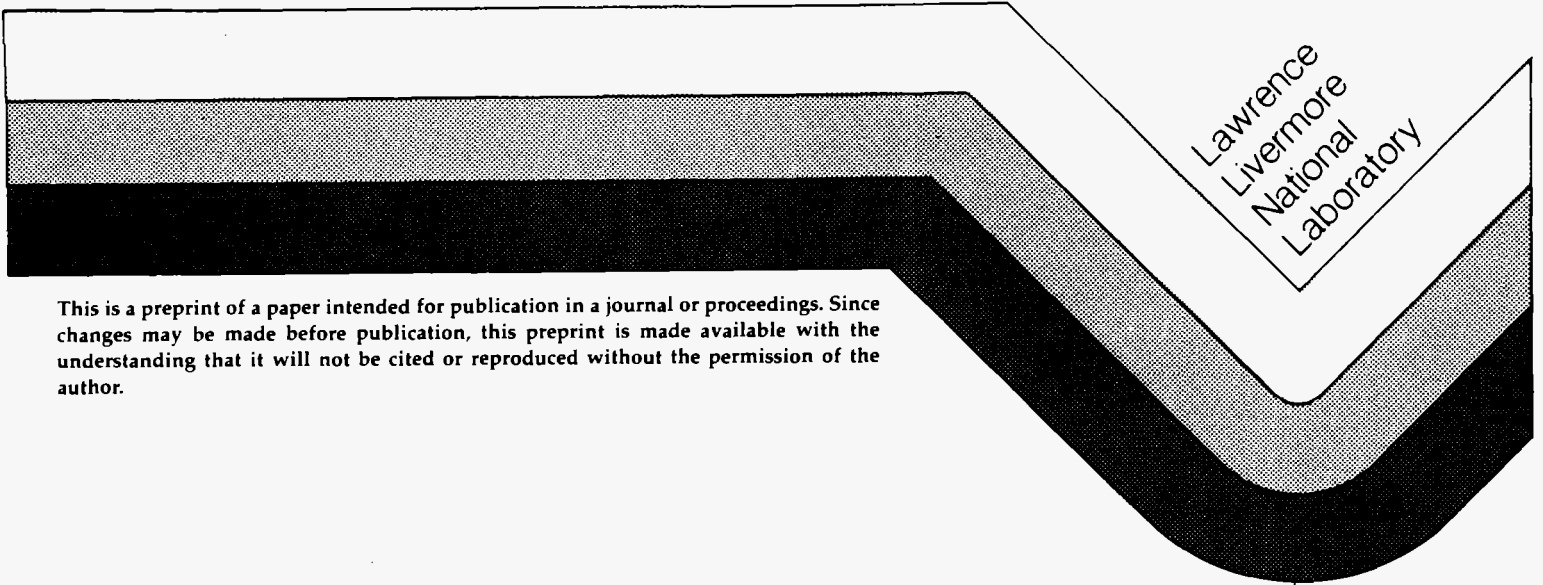


INTERPRETATION OF SELF-POTENTIAL ANOMALIES
USING CONSTITUTIVE RELATIONSHIPS FOR
ELECTROCHEMICAL AND THERMOELECTRIC
COUPLING COEFFICIENTS

R. B. Knapp
P. W. Kasameyer

This paper was prepared for submittal to
Geophysics

February 1988



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

INTERPRETATION OF SELF-POTENTIAL ANOMALIES USING CONSTITUTIVE RELATIONSHIPS FOR ELECTROCHEMICAL AND THERMOELECTRIC COUPLING COEFFICIENTS

R. B. Knapp and P. W. Kasameyer

Lawrence Livermore National Laboratory, PO Box 808, Livermore, California 94550

ABSTRACT

Constitutive relationships for electrochemical and thermoelectric cross-coupling coefficients are derived using ionic mobilities, applying a general derivative of chemical potential and employing the zero net current condition. The general derivative of chemical potential permits thermal variations which give rise to the thermoelectric effect. It also accounts for nonideal solution behavior. An equation describing electric field strength is similarly derived with the additional assumption of electrical neutrality in the fluid (Planck approximation). The Planck approximation implies that self-potential (SP) is caused only by local sources and also that the electric field strength has only first order spatial variations.

The derived relationships are applied to the NaCl-KCl concentration cell with predicted and measured voltages agreeing within 0.4 mV. The relationships are also applied to the Long Valley and Yellowstone geothermal systems. There is a high degree of correlation between predicted and measured SP response for both systems, giving supporting evidence for the validity of the approach. Predicted SP amplitude exceeds measured in both cases; this is a possible consequence of the Planck approximation. Electrochemical sources account for more than 90% of the predicted response in both cases while thermoelectric mechanisms account for the remaining 10%; electrokinetic effects are not considered. Predicted electrochemical and thermoelectric voltage coupling coefficients are comparable to values measured in the laboratory.

The derived relationships are also applied to arbitrary distributions of temperature and fluid composition to investigate the geometric diversity of observed SP anomalies. Amplitudes predicted for hypothetical saline spring and hot spring environments are less than 40 mV. In contrast, hypothetical near surface steam zones generate very large amplitudes, over 2 V in one case. These results should be viewed with some caution due to the uncertain validity of the Planck approximation for these conditions. All amplitudes are controlled by electrochemical mecha-

nisms. Polarities are controlled by the curvature of the concentration or thermal profile. Concave upward thermal profiles produce positive anomalies, for constant fluid concentrations, whereas concave upward concentration profiles produce negative anomalies. Concave downward concentration profiles are characterized by small negative closures bounding a larger, positive SP anomaly.

INTRODUCTION

Naturally occurring self-potential differences (SP) are caused by electrokinetic, thermoelectric and electrochemical processes. Electrokinetic sources are caused by a flowing, electrically imbalanced fluid; electrical imbalance is most often caused by preferential cation adsorption onto certain mineral surfaces (Ishido and Mizutani, 1981; Nourbehecht, 1963; Shaw, 1980). Electrokinetic processes are commonly considered to be one of the primary causes of SP in geothermal areas (Anderson and Johnson, 1976; Corwin *et al*, 1981; Corwin and Hoover, 1979; Ishido *et al*, 1987; Zablocki, 1975; Zohdy *et al*, 1973), in earthquake epicentral regions (Corwin and Morrison, 1977; Fitterman, 1978) and in some engineering applications (Ahmad, 1964; Bogoslovsky and Ogilvy, 1973; Nourbehecht, 1963; Ogilvy *et al*, 1969; Tuman, 1963). Anomalies from several tens of mV to 1600 mV have been numerically or conceptually modeled by assuming an electrokinetic mechanism.

Thermoelectric processes originate from thermally induced diffusion in aqueous electrolytes (Bockris and Reddy, 1973; de Groot and Mazur, 1984; Fitts, 1962; Nourbehecht, 1963). They are often considered to be an important SP source in geothermal areas (Corwin *et al*, 1981; Corwin and Hoover, 1979; Fitterman and Corwin, 1982; Fitterman, 1984). Anomalies as large as 160 mV have been modeled assuming this source.

Electrochemical processes originate from isothermal aqueous diffusion (Bockris and Reddy, 1973; de Groot and Mazur, 1984; Fitts, 1962; Nourbehecht, 1963). These are usually discounted as significant SP sources, except in mineralized areas, due to the common belief that they contribute less than about 20 mV to observed anomalies (Corwin and Hoover, 1979; Nourbehecht, 1963; Sato and Mooney, 1960; Telford *et al*, 1976). This is in contrast to the importance of electrochemical processes in well-logging (Hearst and Nelson, 1985) and to the conclusions drawn by Gay (1967) and Kruger and Lacy (1949) when explaining 1,800 mV and 700 mV SP anomalies over altered rock. We have excluded oxidation-reduction mechanisms discussed by Kilty (1984) and Sato and Mooney (1960).

Interpretation of SP field surveys has been predominantly through the total potential approach developed by Nourbehecht (1963) and refined by Fitterman (1979; 1983). Sill (1983) has advanced interpretation with a technique that explicitly models primary flows and secondary potentials and facilitates more realistic distributions of material properties. However, application of either technique is inhibited by poor knowledge of both *in situ* conditions and the appropriate coupling coefficients. Quantitative modeling almost invariably treats coupling coefficients like a dependent variable which is adjusted until a good match between measured and predicted SP is achieved. The resultant coupling coefficients are usually much larger, often by an order of magnitude, than laboratory measurements would indicate is reasonable (Corwin *et al* , 1981; Fitterman and Corwin, 1982; Sill, 1983). Interpretation of source mechanisms remains quite ambiguous, especially in geothermal areas where all three processes may contribute and where anomalies occur with a multiplicity of magnitudes, polarities and spatial extents.

The use of coupling coefficients as iteration variables is, in part, caused by their sensitivity to changes in temperature, fluid composition and rock type (Fitterman and Corwin, 1982; Ishido and Mizutani, 1981; Nourbehecht, 1963). This multifarious behavior requires that either an extensive experimental data base or constitutive relationships be developed for less ambiguous interpretation. Effective constitutive relationships do exist for electrokinetic phenomena (Ishido and Mizutani, 1981; Tuman, 1963).

Our current objective is to develop constitutive relationships that permit calculation of electrochemical and thermochemical coupling coefficients from a knowledge of temperature and bulk fluid composition. We apply these relationships to field areas where there is sufficient knowledge of *in situ* conditions to calculate their values and we show that electrochemical processes appear to dominate in several field areas.

CONSTITUTIVE RELATIONSHIPS

Much of the recent quantitative modeling and interpretation of SP has centered around a modified Onsager phenomenological equation (Fitterman, 1978, 1979 and 1983; Fitterman and Corwin, 1982; Nourbehecht, 1963; Sill, 1983)

$$\mathbf{J}_T^* = -L^{ee}\mathbf{E} - L^{eT}\nabla T - \sum_{i=1}^n L_i^{ep}\nabla\rho_i \quad (1)$$

where

- E = electric field strength (N/C)
 J_T^* = total charge flux (C/m²/s)
 L^{ee} = primary electrical conductivity (C²/N/m²/s)
 L^{eT} = cross coupling coefficient relating a thermal gradient to an electrical current (C/°K/m/s)
 L_i^{ep} = cross coupling coefficient relating a concentration gradient to an electrical current (C·m³ solution/kg/m/s)
 n = total number of aqueous species
 T = temperature (°K)
 ρ_i = concentration of i th aqueous species (kg/m³ solution)

In equation (1) the coefficients relate gradients in measurable field variables to the electric current, giving them a somewhat different interpretation than in a formal Onsager equation. We start with basic chemical principles and derive constitutive relationships for these coefficients in terms of physical constants, intrinsic ion properties, media properties and state variables.

Constitutive relationships have been previously developed for electrochemical coupling coefficients (Bockris and Reddy, 1973; de Groot and Mazur, 1984; Fitts, 1962; Nourbehecht, 1963; Robinson and Stokes, 1959). All are variants of the Planck-Henderson equation; this assumes isothermal conditions, ideal solution and linear chemical potential gradients, and is the equation usually quoted in geophysical texts (Hearst and Nelson, 1985; Telford *et al*, 1976). We develop a more general equation starting with the approach used by Robinson and Stokes (1959) and Wendt (1965) for modeling diffusion coefficients.

The macroscopic mass flux of an aqueous species can be described by

$$J_i = \phi \rho_i u_i \left[ez_i E - \frac{\nabla \mu_i}{N_0} \right] \quad (2)$$

where

- e = protonic charge (C)
- \mathbf{J}_i = mass flux of i th aqueous species ($\text{kg}/\text{m}^2/\text{s}$)
- N_0 = Avogadro's number (per mole)
- u_i = intrinsic mobility of i th aqueous species
($\text{m}/\text{s}/\text{N}$)
- z_i = valence of i th aqueous species
- μ_i = chemical potential of i th aqueous species
($\text{N}\cdot\text{m}/\text{mole}$)
- ϕ = porous media term

For any aqueous solution, n equation (2)'s can be written, one for each aqueous species present. Equation (2) treats each species as a separate and distinct variable. This is in contrast to the formal Onsager mass flux equation which is written in terms of chemical components. Components are the smallest, independent set of elements or combinations of elements that span the chemical composition of the fluid; components often do not correspond to any actual chemical entity. Species, on the other hand, are actual chemical entities statistically present in the fluid; these often greatly outnumber the chemical components. This approach expands the computational effort because the number of aqueous species present in most natural solutions greatly exceeds the number of chemical components, thereby increasing the number of equations to solve. It also produces a dependency between the chemical and thermal driving forces as will be discussed later.

The remaining development expands the chemical potential gradient in terms of temperature, concentration, constants and intrinsic ion variables. We reference chemical potential to a standard state at any temperature and pressure at infinite dilution; it is corrected for real solutions through a chemical activity term

$$\mu_i = \mu_i^0(T,P) + RT \ln a_i \quad (3)$$

where

- a_i = activity of i th species
- R = gas constant
- $\mu_i^0(T,P)$ = standard state chemical potential of i th species; a function of temperature and pressure

The activity,

$$a_i = \gamma_i m_i \quad (4)$$

accounts for ion-ion and ion-solvent interactions, through the activity coefficient, γ_i (kg H₂O/mole i), which can either reduce or increase the effective concentration. Molality, m_i (moles i/kg H₂O), can be transformed to units more conventional in transport theory by assuming that aqueous species have a negligible influence on solution volume

$$m_i \approx \frac{\rho_i}{W_i \rho_{H_2O}} \quad (5)$$

where

W_i = molecular weight (kg / mole)

$\alpha(T)$ = coefficient of thermal expansion for water

ρ_{H_2O} = density of water (kg / m³)

Taking the derivative of (3) at constant pressure, applying (4) and (5) and substituting the result into (2) yields

$$\begin{aligned} J_i = & [\phi \rho_i u_i e z_i] E - \left[\frac{\phi \rho_i u_i}{N_0} \right] \left\{ \frac{d \mu_i^0(T)}{dT} + R [\ln \gamma_i + \ln \rho_i - \ln W_i - \ln \rho_{H_2O}] + \right. \\ & \left. [R T \alpha(T)] \left[1 + \frac{\rho_i}{W_i \rho_{H_2O} \gamma_i} \frac{\partial \gamma_i}{\partial m_i} \right] \right\} \nabla T - \\ & \left[\frac{R T \phi \rho_i u_i}{N_0} \right] \left[\frac{1}{\rho_i} + \frac{1}{W_i \rho_{H_2O} \gamma_i} \frac{\partial \gamma_i}{\partial m_i} \right] \nabla \rho_i \quad (6) \end{aligned}$$

The approach using actual aqueous species instead of chemical components results in a dependency between temperature, T , and species concentration, ρ_i . This dependency is a consequence of thermodynamic equilibrium within the fluid, is a relatively small effect and can cause confusion when interpreting laboratory measured coupling coefficients. In an aqueous solution, chemical components are distributed between several compounds - aqueous species.

The relative abundance of each species is controlled by an equilibrium constant which is largely a function of temperature. At low temperatures, components occur predominantly in dissociated species, like Na^+ , but as temperature increases so does the relative abundance of the associated forms, like NaCl . This change in internal solution equilibrium modifies the charge of migrating species and directly effects the current, even for equivalent driving forces. However, this effect is expected to be less than several mV for most situations.

Laboratory measurements of thermoelectric coefficients are usually conducted with a constant bulk composition fluid and an applied thermal gradient. This applied thermal gradient induces gradients in species concentrations and results in, using the current derivation, a small electrochemical effect. Models written with respect to chemical components (eg. Anderson and Graf, 1978) have a complete independency between the state variables and would interpret the laboratory experiments as measuring thermoelectric effects only. Our method complicates interpretation while elucidating concurrent chemical and thermal phenomena.

The total charge flux, or current, is linearly related to the mass flux by

$$\mathbf{J}_T^* = \sum_{i=1}^n \frac{F z_i}{W_i} \mathbf{J}_i \quad (7)$$

where

F = Faraday's constant (C / mole)

Expressions for the cross-coupling coefficients can be written by substituting (6) into (7) and comparing the result with (1)

$$L^{\infty} = - e F \phi \sum_{i=1}^n \frac{z_i^2 \rho_i u_i}{W_i} \quad (8)$$

$$L^{eT} = \left[\frac{F \phi}{N_0} \right] \sum_{i=1}^n \left[\frac{z_i \rho_i u_i}{W_i} \right] \left\{ \frac{d \mu_i^0(T)}{dT} + R \left[\ln \gamma_i + \ln \rho_i - \ln W_i - \ln \rho_{\text{H}_2\text{O}} \right] + \right.$$

$$[R T \alpha(T)] \left[1 + \frac{\rho_i}{W_i \rho_{H_2O} \gamma_i} \frac{\partial \gamma_i}{\partial m_i} \right] \quad (9)$$

$$L_i^{ep} = \left[\frac{F R T \phi}{N_0} \right] \left[\frac{z_i \rho_i u_i}{W_i} \right] \left[\frac{1}{\rho_i} + \frac{1}{W_i \rho_{H_2O} \gamma_i} \frac{\partial \gamma_i}{\partial m_i} \right] \quad (10)$$

These coefficients are complex functions of constants, state variables, intrinsic ion variables and the activity coefficient. The activity coefficient can also be expanded into constants, state variables and intrinsic ion variables by applying the Debye-Huckle relationship (Robinson and Stokes, 1959).

Nourbehecht's (1963) expression for primary electrical conductivity and (8) are identical when expressed in equivalent units. The multiplicity of terms in (9) and (10) explains some of the diverse behavior reported in the literature for these coefficients (Dorfman *et al*, 1977; Fitterman and Corwin, 1982).

The unequal mobilities of cations and anions causes a net charge flux upon the initiation of a chemical potential gradient. However, the electrical imbalance caused by this current initiates a counter force which results in a zero net current condition after about a nanosecond (Hafemann, 1965; MacGillivray, 1967; Leckey and Horne, 1981). Therefore, for time frames of geophysical interest, for slowly varying gradients and for no external sources

$$\nabla \cdot \mathbf{J}_T^* \equiv 0 \quad (11)$$

and

$$L^{ee} \nabla \cdot \mathbf{E} + \nabla L^{ee} \cdot \mathbf{E} = - \sum_{i=1}^n L_i^{ep} \nabla^2 \rho_i - \sum_{i=1}^n \nabla L_i^{ep} \cdot \nabla \rho_i - L^{eT} \nabla^2 T - \nabla L^{eT} \cdot \nabla T \quad (12)$$

It is at this point that standard geophysical practice deviates from standard electrochemical practice. Since Planck in 1890, it has been standard electrochemical practice to assume electrical neutrality in the solution and, via Gauss' Law, eliminate the divergence of the electrical field strength. In contrast, it is this term that potential methods seeks

to solve. We will use the Planck approximation and solve (12) for the magnitude of E colinear to ∇L^{ee} , assuming of course that ∇L^{ee} is not equal to zero. Then

$$|E| = - \sum_{i=1}^n \frac{L_i^{ep}}{|\nabla L^{ee}|} \nabla^2 \rho_i - \sum_{i=1}^n \frac{\nabla L_i^{ep}}{|\nabla L^{ee}|} \nabla \rho_i - \frac{L^{eT}}{|\nabla L^{ee}|} \nabla^2 T - \frac{\nabla_x L^{eT}}{|\nabla L^{ee}|} \nabla T \quad (13)$$

Thus, the Planck approximation implies that the electric field depends only on the values and spatial derivatives of fluid chemistry and temperature at the point of interest. This conclusion contrasts with the normal geophysical application of SP measurements to study subsurface processes.

Application of the electroneutrality approximation leads to several discrepancies and an unfortunate characteristic of the governing equation (13). First and foremost, aqueous solutions experiencing a chemical potential gradient are not electrically neutral. The current in the first nanosecond upon application of a gradient establishes an electrical imbalance that is sustained until diffusion eliminates the gradient (Mafe *et al*, 1986; Aguilera *et al* 1987; Mafe *et al*, 1986; 1987). The imbalance is caused by an excess mass of anions with respect to cations on the order of one part per trillion. This exceedingly small mass imbalance is beyond measurement resolution at this time. We note that this electrical imbalance is separate and distinct from imbalances caused by preferential adsorption of cations onto mineral surfaces. Thus it is an additional, and previously unreported, source of electrokinetic potentials.

The second discrepancy is that the electric field calculated from equation (13) will have spatial variations, which is inconsistent with the Planck approximation. This discrepancy has been noted in the electrochemical literature previously cited.

Examination of equation (13) reveals that the gradient of the conductivity, L^{ee} , appears in the denominator. Thus equation (13) becomes undefined for homogeneous fields and at extrema in net concentration and temperature. This unfortunate characteristic limits the usefulness of the simple form of equation (13).

The ultimate justification for use of the Planck approximation is in comparison of calculated results with measured values. We will next show that predicted voltages are in reasonable agreement with measured voltages for a laboratory case and two field cases. In addition, calculated thermoelectric coupling coefficients are in agreement with laboratory measured values.

Equation (13) is significantly different than the form of the Planck-Henderson equation which frequently appears in geophysical texts (eg. Telford *et al*, 1976) In particular, (13),

1. incorporates nonideal solution behavior through the activity coefficient
2. includes thermal variations which explicitly give rise to the thermoelectric effect
3. permits nonlinear gradients in chemical potential
4. uses (11) as opposed to the more common condition of equal and opposite anion and cation fluxes, a special case of (11)

This last difference appears to be most important. Expressions for the coefficients, (8)-(10), were derived using (14) and applied to the following field examples. Calculated results differed significantly from observed SP, in contrast to the present derivation which gave excellent correlation between calculated and observed SP.

Equation (13) contains second as well as first derivatives, indicating the curvature of thermal and concentration variations will influence SP. It will be shown that this contributes to the polarity of SP anomalies.

Several authors have modeled diffusion coefficients using different approaches than the current one (Anderson and Graf, 1978; Miller, 1966; 1967a; 1967b). The most accurate model is by Anderson and Graf (1978) who apply transition-state theory. Their predictions match experimental values within about 5% for most cases; the Wendt (1965) approach gives errors around 10% for simple, dilute solutions and errors close to 20% for more complex and concentrated solutions. The current approach is an improvement upon the Wendt (1965) model, by incorporating nonideal solution behavior, through Debye-Huckle theory, and by applying condition (11); we anticipate our results to be intermediate in accuracy to the Wendt (1965) and Anderson and Graf (1978) models.

INTRINSIC ION DATA BASE

The derived coupling coefficients, (8) through (10), are functions of intrinsic ion properties, u_i , W_i , z_i and μ_i^0 ; of these, W_i and z_i are constants. The absolute mobility, u_i , is the velocity of an ion when experiencing a unit force; it is a function of temperature, pressure, solution composition and concentration (Bockris and Reddy, 1973; Robinson and Stokes, 1959). The addition of other ions in solution usually retard velocity due to ion-ion electrical interactions. These interactions are complex and difficult to predict and so the mobility at infinite dilution is often employed. Use of limiting mobilities decreases the generality of (8) - (10) because we would expect them to

increasingly deviate from measured values as solutions become more concentrated, *ie.* greater than about 1 molal.

This feature is moderated to a degree by our use of activity coefficients which account for ion-ion interactions.

Nigrini (1970) has developed a correspondence principle which permits calculation of absolute mobilities from 25°C to 300°C using limiting equivalent ionic conductances. This principle has been applied to generate mobili

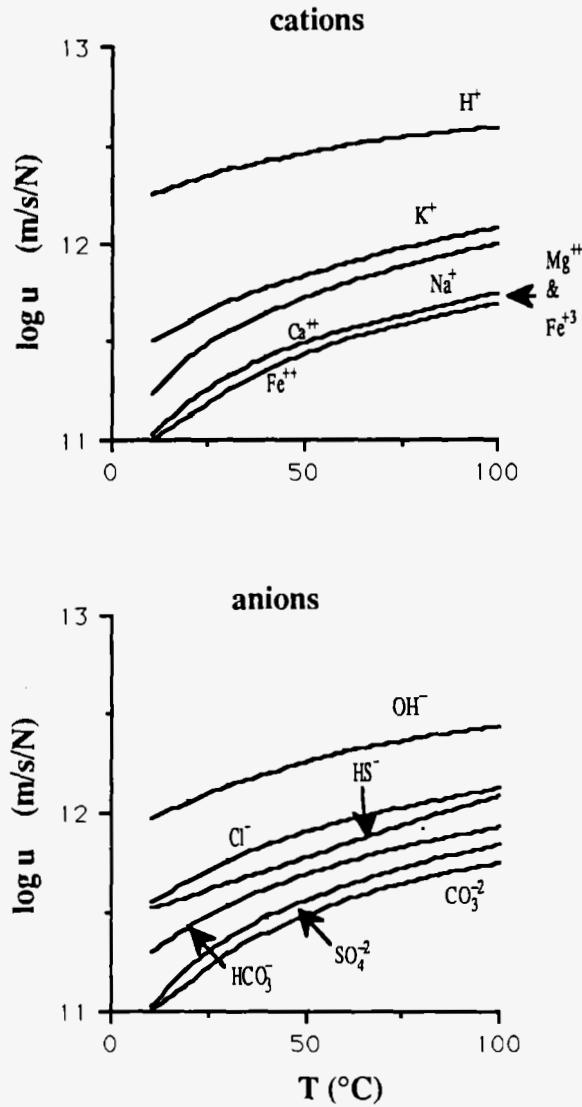


Figure 1. Limiting, absolute mobilities calculated using Nigrini's (1970) correspondence principle. Bicarbonate mobility is estimated. Hydrogen and hydroxide have extraordinarily high mobilities but their contribution to E is reduced by their low concentration in solution. All species experience an increase in mobility by about a factor of 5 as temperature increases from 25°C to 100°C.

TABLE 1: $\frac{\partial \mu_i^0}{\partial T}$ from 10°C to 100°C and 0.1 MPa

Ca ⁺²	53.4	Cl ⁻	- 48.2	(N m/°K)
Fe ⁺²	102.7	Fe ⁺³	271.4	
H ⁺	0.0	HCO ₃ ⁻	- 96.8	
HS ⁻	- 54.3	K ⁺	- 103.8	
Mg ⁺²	133.6	Na ⁺	- 64.3	

ties for the major ions (figure 1). Bicarbonate mobility has been approximated by assuming that the carbonate to bicarbonate mobility ratio is proportional to the sulfate to bisulfate mobility ratio. Most species have mobilities in the 10¹¹ (m/s/N) to 10¹² (m/s/N) range. OH⁻ and especially H⁺ have considerably greater mobilities. However, their extremely small concentration in solution reduces their contribution to SP.

μ_i^0 by convention (Helgeson *et al*, 1981) is the partial molal Gibbs free energy at unit activity referenced to infinite dilution at any temperature and pressure. For most of the species in figure 1, μ_i^0 experiences linear changes with temperature; the change is positive for multivalent cations and negative for univalent cations and most of the anions (Helgeson *et al*, 1981). Temperature derivatives for these are simple constants (Table 1). Hydroxide and sulfate are different in that their relationship to temperature is second order, giving linear temperature derivatives (figure 2).

VALIDATION

The governing equation, (13), and the constitutive relationships for the coefficients, (8) - (10), have been applied to a NaCl-KCl concentration cell using concentration profiles reported in Hafemann (1965). This laboratory experiment is inherently one-dimensional and so (13) should give a reasonable value if the Planck approximation is valid. Voltage calculated from (13) using Romberg integration is 6.86 mV which is in good agreement with the laboratory measured value of 6.42 mV. Our calculated voltage appears to be the best reported prediction of voltage for this cell; most other predictions lie within the 4-5 mV range. The success of the calculation is supporting evidence for the validity of (13) and the Planck approximation.

Equation (13) has also been applied to two field areas where measured SP, surficial temperatures and surficial solution compositions are available. Knowledge of these variables permit calculation of all coefficients and deriva

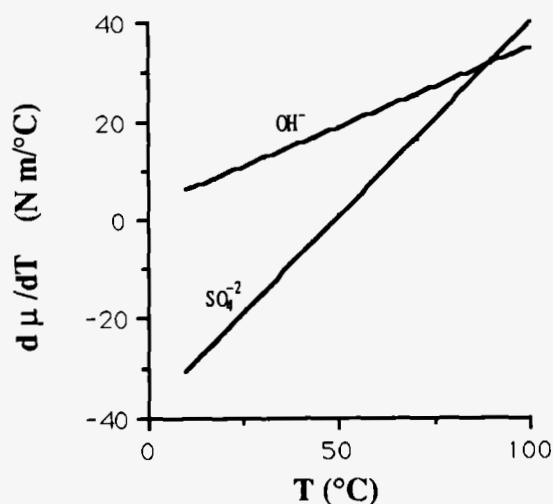


Figure 2. Temperature derivative of the standard state chemical potential for hydroxide and sulfate (Helgeson *et al.*, 1981). These two species have linear derivatives as opposed to the constant derivatives of the other species used in this study.

tives and direct computation of SP profiles through numerical integration of (13). Self-potentials predicted in this manner can be directly compared with measured values to assess the validity of (13) and to interpret the relative importance of the various processes. We demonstrate a high degree of correlation between predictions and observations and conclude that, for the two cases studied, electrochemical processes are the main SP generating mechanism.

Long Valley

A field SP survey was conducted in Long Valley, California to test the validity of (13) in a field situation; this location was chosen because of the abundance of available fluid compositional and temperature data. The line is from Whitmore Hot Springs to 1 km north along a road. Temperatures and fluid compositions at each of the 7 stations are interpolated from the 5 hot springs and 1 cold spring in a three kilometer radius. Maximum temperature is about 50°C and sodium is the major cation while bicarbonate is the major anion (Lewis, 1974; Mariner and Willey, 1976; Sorey and Lewis, 1976; Willey *et al.*, 1976). SP is calculated using finite difference derivatives and numerical integration of (13).

There is a high degree of correlation between predicted and measured SP (figure 3); the geometries are strikingly similar. This near congruency is additional supporting evidence for the general validity of the governing equation,

(13). There is a large difference in amplitudes, however; the maximum predicted peak-to-trough amplitude is about 55 mV larger than that observed. This error could be due to

1. ignoring vertical thermal and compositional variations,
2. deviations of E and ∇L^{ee} from colinearity,
3. a breakdown in the Planck approximation and
4. the possible importance of electrokinetic effects, which are not considered

SP data collected in the vicinity by Anderson and Johnson (1974) suggest a regional 30 mV/km gradient. This is approximately the voltage required for the predicted values to match measured values, supporting a breakdown in the Planck approximation as a possible cause of the discrepancy.

We have modeled this field example by assuming that thermoelectric and electrochemical sources are the only ones acting. Further analysis shows that electrochemical forces account for about 90% of the computed anomaly. Computed thermoelectric voltage coupling coefficients range between 0.3 and 0.8 mV/°C. This is in good agree

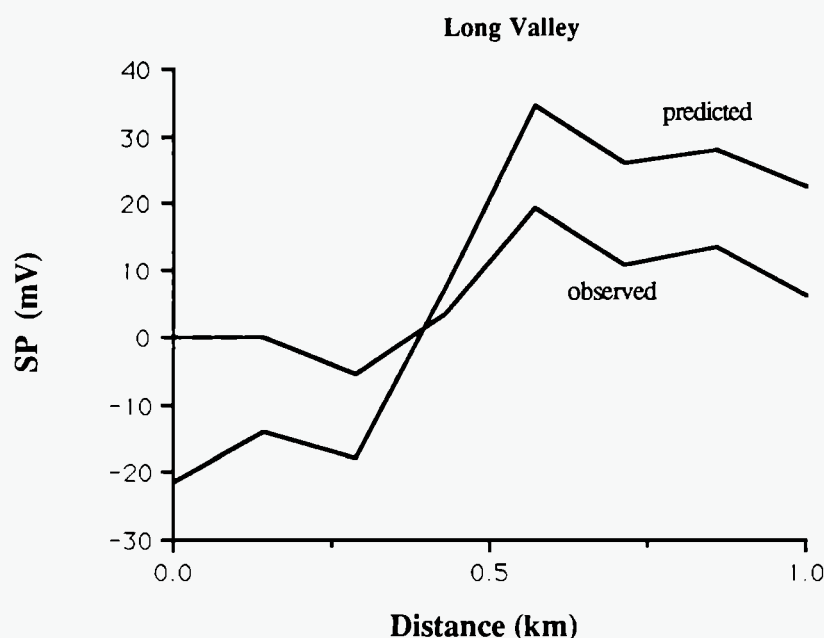


Figure 3. A comparison between SP profiles predicted by (13) and measured at the Whitmore Hot Springs area, Long Valley, California. State variables in (13) were computed using data from 6 springs in the area of the measured SP line. The congruency between the curves is compelling evidence for the validity of (13), even though the predicted amplitude is about 3 times the observed magnitude. Electrochemical sources account for about 90% of this particular anomaly.

ment with laboratory values which appear to range from (-) 0.25 to (+) 1.4 mV/°C (Nourbehecht, 1963; Dorfman *et al*, 1977; Fitterman and Corwin, 1983). There is a closer agreement between the chemical driving force and computed SP than for the thermal gradient, though both display some similarities (figure 4).

The Long Valley case is not a particularly stringent test of the general importance of electrochemical sources. It is accepted that electrochemical sources are capable of producing an anomaly of this small magnitude but not much

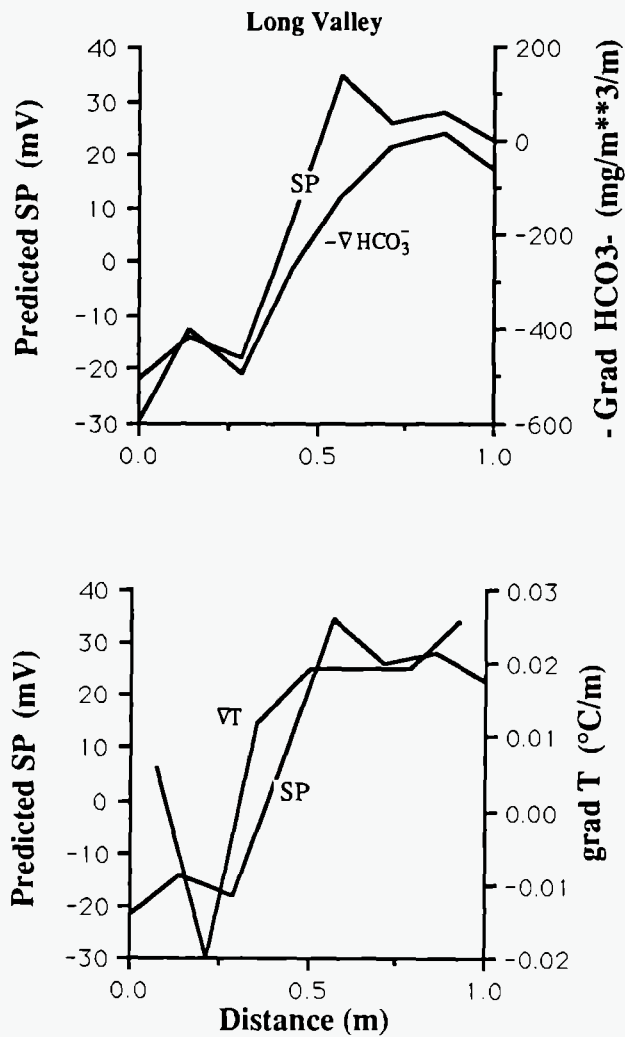


Figure 4. The major source for predicted SP at Long Valley is electrochemical, which accounts for about 90% of the anomaly. Bicarbonate is the major species and its variation appears to control SP. There is also a good correlation between the thermal gradient and predicted SP, though it is generally not as good as the chemical correlation. Computed thermoelectric voltage coupling coefficients agree with laboratory measured values.

greater (Corwin and Hoover, 1979; Nourbehecht, 1963; Sato and Mooney, 1960; Telford *et al*, 1976). We next model a survey of greater amplitude in an effort to further validate the governing equation, (13), and to gain increased insight into the general importance of electrochemical sources.

Yellowstone

Self-potential was predicted from (13) for the Mud Volcano area, Yellowstone, Wyoming using spatial temperature and fluid compositional data from the literature (White *et al*, 1971; Zohdy *et al*, 1973). The data are sparse and some inferences have been made (figure 5). The temperature profile is inferred and a constant 100°C temperature has been chosen to represent the near surface steam zone. interpreted by White *et al* (1971) and Zohdy *et al* (1973). The fluid compositional profiles have been assigned by assuming the steam zone is highly dilute, using data from drill-hole Y-11 to represent fluid adjacent to the steam zone and then employing a background fluid composition for the far-field; sulfate and sodium are diagnostic of the inferred spatial variations in fluid composition.

Predicted SP displays a high correlation with SP measured by Zohdy *et al* (1973), (figure 5). The broad decreasing then increasing trend is predicted, though the peak-to trough magnitude, about 70 mV, is greater than that measured, about 50 mV. The resolution of the predictions is less due the relative sparseness of the measured state variables. Electrochemical sources again account for more than 90% of the predicted SP response.

Conclusions

Taken in concert, the excellent agreement between predicted and measured voltage for the NaCl-KCl cell and the high degree of correlation between predicted and measured SP in the two field areas is compelling evidence for the validity of the governing equations, (8)-(10) and (13), and for the potential importance of electrochemical sources. SP trends can be successfully approximated in geothermal environments solely through electrochemical mechanisms, at least in these two cases; we have not included electrokinetic mechanisms in our calculations and have demonstrated the secondary importance of thermoelectric effects.

However, predicted amplitudes are larger than measured amplitudes in both field cases. This feature is not understood but could be caused by our use of the Planck approximation. This approximation assumes that the electric field strength is divergenceless whereas examination of figures 3 and 5 shows that it is not. In addition the

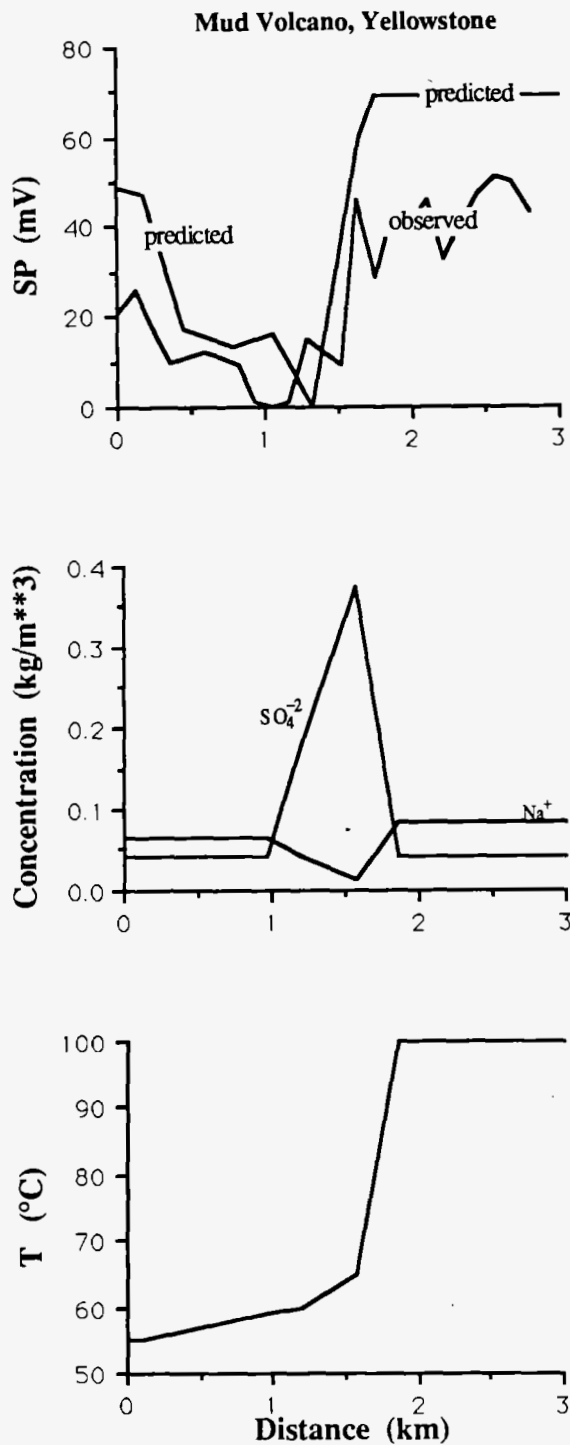


Figure 5. Data from the Mud Volcano area, Yellowstone, Wyoming, used to generate a predicted SP profile which is compared with a measured curve. This area is characterized by a near-surface steam zone with neutral, sulfate-bicarbonate solutions on its boundaries. Sulfate and sodium are diagnostic of inferred compositional changes. The close congruency between predicted and measured SP supports the validity of (8)-(10) and (13).

approximation precludes regional sources from consideration; these regional sources could account for differences in magnitude between predicted and measured SP. If this is true, then our current approach permits local electrochemical sources to be filtered from the overall signal.

The calculations also show that electrochemical sources arising from natural variations in fluid compositions can generate SP responses of greater magnitude than is commonly considered possible. While the applications discussed above support the validity of the governing equation, the geological settings and SP responses are fairly limited. Self-potential measured in the field displays a diversity of magnitudes and polarities in a variety of settings. In the following section we apply the equations to arbitrary distributions of temperature and fluid compositions. The purpose of these heuristic examples is two-fold: to determine the capability of the governing equation to produce a variety of SP profiles and to gain insight into possible causes for observed SP features

EXAMPLES

The constitutive relationships, (8)-(10), and the governing equation, (13), describe the dependency of self-potential on fluid composition, temperature and their derivatives. In this section we arbitrarily assign values to the state variables and their derivatives to generate synthetic SP profiles. This procedure facilitates understanding of how thermoelectric and electrochemical processes act individually and in concert to produce anomalies of differing amplitude and polarity. We emphasize that we are applying (13) to conditions where the validity of the Planck approximation has not been verified; results and conclusions should be viewed with caution because of this uncertainty.

The influence of temperature on SP is investigated by arbitrarily selecting a background temperature of 15 °C and a maximum temperature of 100 °C. Three spatial variations are also used (figure 6): isothermal (T1), concave upward (positive second derivative, T2) and concave downward (T3).

The influence of fluid compositional variations on SP is examined by using two natural solutions: a dilute fluid as background, from Champagne Pool, Wairakei, N. Z. (Ellis and Mahon, 1977) and a saline solution from Long Valley (Lewis, 1974). Equilibrium species concentrations at the thermal extremes are given in Table 2. Selected spatial variations are (figure 6) saline-isogramal (ρ_1), and a saline spring (Long Valley solution) flowing into a dilute background (ρ_2 and ρ_3). ρ_2 and ρ_3 differ in the sign of the second derivative: ρ_2 is concave upward whereas ρ_3

TABLE 2: Example Fluid Compositions (kg/m³)

	Wairakei			Long Valley	
	15. °C	100. °C		15. °C	100. °C
Cl ⁻	1.810	1.780	Cl ⁻	7.990	7.730
K ⁺	0.106	0.102	K ⁺	0.005	0.005
Na ⁺	1.110	1.070	Na ⁺	25.000	24.000
			Ca ⁺²	10.800	8.650
			CO ₃ ⁻²	0.125	0.188
			HCO ₃ ⁻	100.000	90.600
			Mg ⁺²	10.800	8.650
			SO ₄ ⁻²	8.050	7.350

is concave downward. These spatial variations are completely arbitrary and independent of the thermal variations; this results in a small disequilibrium condition when T2 or T3 are combined with ρ_1 , ρ_2 or ρ_3 .

Combinations of the three thermal variations and three compositional variations permit simulation of individual and coupled processes. The conditions can also be viewed as approximating different geologic settings. For example, T1- ρ_2 and T1- ρ_3 represent isothermal saline springs while T2 and T3 combinations represent different types of hot springs. We now examine the different combinations.

SP amplitudes for isothermal conditions (T1- ρ_2 and T1- ρ_3) are less than about 40 mV; amplitudes for isogramal conditions (T2- ρ_1 and T3- ρ_1), are smaller, being about 20 mV. Computed thermoelectric voltage coupling coefficients are in the (-) 0.1 to (+) 0.2 mV/°C range, consistent with laboratory measurements. Computed electrochemical voltage coupling coefficients are in the (-) 15 to (+) 10 mV/decade-increase-in-chloride-concentration range; this is close to the range measured by Nourbehecht (1963) using NaCl solutions, (-) 6 to (+) 46 mV/decade.

For the selected conditions, combined electrochemical and thermoelectric effects produce anomalies smaller than pure electrochemical anomalies; for case T3- ρ_3 the two effects combine to produce a nearly null response. It should be noted that anions, especially the dominant one, control the electrochemical contribution. Anions occur in most natural solutions with greater mass densities (kg/m³ solution) because their molecular weights are, in general, greater than the molecular weights of cations.

Polarity of computed SP is consistently controlled by the curvature of the thermal or concentration variations, but the control is opposite for the two sources. Positive curvature for temperature produces a positive anomaly (T2-

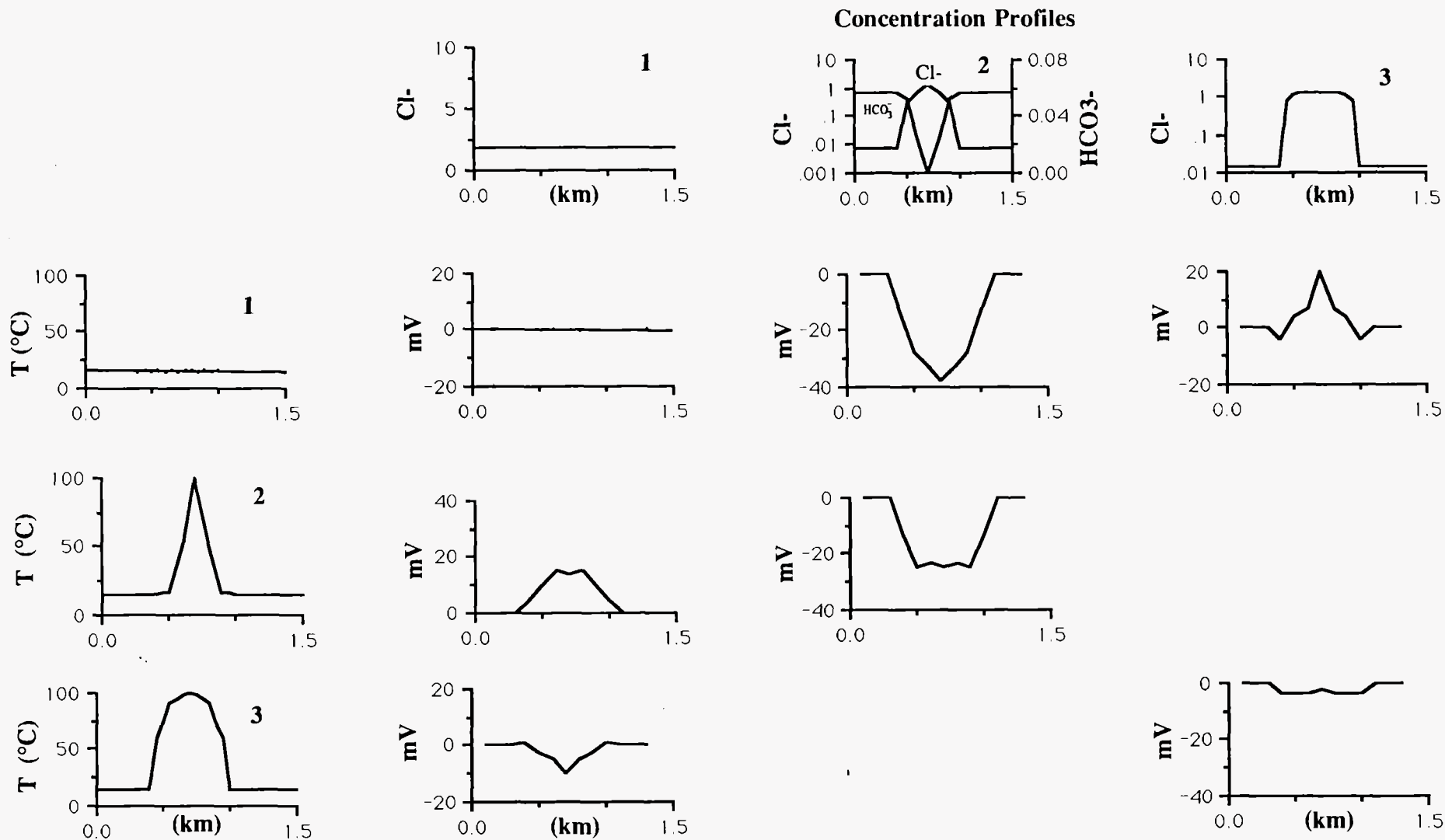


Figure 6. Predicted SP response for hypothetical spatial distributions of temperature (T , $^\circ\text{C}$) and concentration (ρ , kg/m^3). Conditions 2 have a concave upward profile, positive second derivative, whereas conditions 3 have a concave downward profile, a negative second derivative. For example, T1-p3 is the response for an isothermal saline spring flowing into a lower concentration environment; T2-p1 is the response for a hot spring where the fluid has the same thermodynamic composition as the surroundings. This case is for illustration purposes only because it represents a physically impossible situation; increasing temperature alters the internal equilibrium state of a solution by increasing the degree of association between aqueous species. All nonisothermal cases in the above SP response matrix represent this same disequilibrium condition. These simple distributions of temperature and concentration give rise to a rich variation in polarity, number of poles and magnitude, though most examples are in the 20 mV range or less; no effort was made to maximize the magnitude. Cases T2-p3 and T3-p2 were not computed.

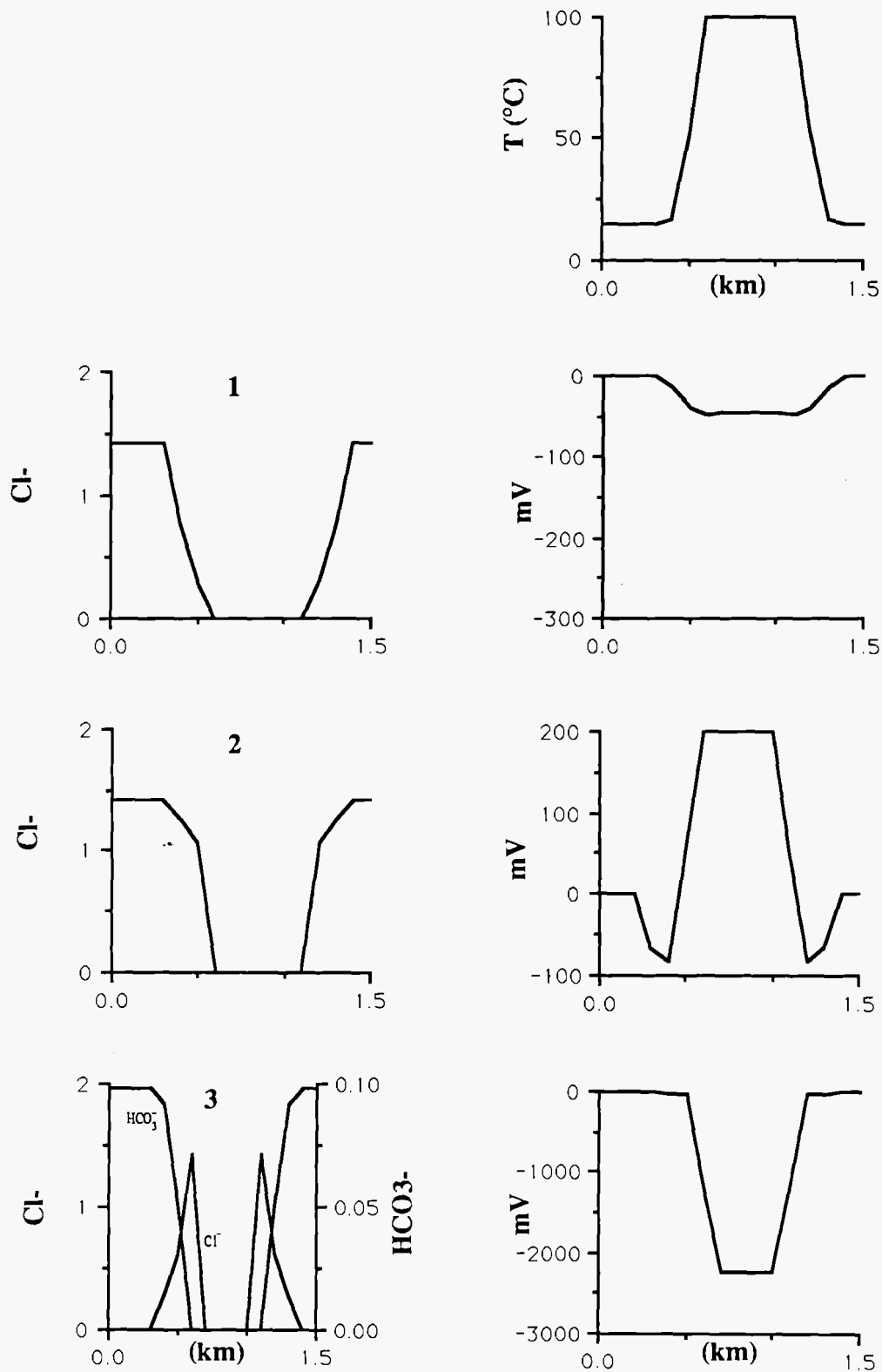


Figure 7. Predicted SP response for a hypothetical temperature distribution (T , °C), meant to represent a shallow steam zone, and hypothetical concentration profiles (ρ , kg/m³). Representative aqueous species are shown. Predicted SP is very large for these cases, over 2V for T-p3, and is consistent with measurements over suspected steam zones (Zablocki, 1975).

ρ_1) whereas a positive concentration curvature causes a negative anomaly (T2- ρ_2 and T3- ρ_2). The high frequency fluctuations in polarity reflect variations in the sign of the second derivative and appear to be diagnostic of concave downward distributions. Concentration variations control the polarity in all of the combined examples.

The amplitude of the above examples are more or less consistent with published expectations of electrochemical anomalies. However, in the following simulation of near surface steam zones we show how very large anomalies can potentially be produced.

We simulate a near surface steam zone by a rapid increase in temperature from a background value, 15 °C, to a plateau characterized by boiling temperatures (figure 7). Three chemical regimes are also simulated, ρ_1 , ρ_2 , ρ_3 , all of which characterize the steam zone as pure H₂O. ρ_1 and ρ_2 differ in the rate the normal groundwater composition approaches pure H₂O while ρ_3 simulates a steam zone bounded by hot, saline fluids flowing into more dilute groundwaters. This last condition might occur as the normal groundwater boils, becomes more concentrated due to the loss of H₂O and then escapes by natural convection to the surface along faults. We again urge caution for these calculations due to the highly uncertain validity of the Planck approximation for these extreme conditions. The results should be viewed as speculative at this time.

The amplitudes of the synthetic SP profiles are surprisingly large, especially for case T- ρ_3 which is over 2 V (figure 7). This large amplitude is a consequence of a similarity in magnitude but opposite signs of the thermal and chemical sources. Zablocki (1975) reports SP amplitudes exceeding 1.5 V over suspected steam zones on Kilauea Volcano, Hawaii. Our calculations suggest an electrochemical source is feasible.

The predicted polarities are again controlled by the concavity of the profile for the dominant anion. T- ρ_2 has the negative closures bounding the central maximum which appear to be diagnostic of concave downward concentration profiles.

CONCLUSIONS

Constitutive relationships for electrochemical and thermoelectric coupling coefficients have been derived from basic chemical principles. These relationships have been applied to two field areas. Excellent correlation between measured and predicted SP and measured and predicted voltage coupling coefficients supports this approach where the Planck approximation is valid.

Interpretation of predicted SP for the two field areas provide evidence for the potential importance of electrochemical sources in natural environments. Thermoelectric sources appear to be secondary in importance while electrokinetic mechanisms were not considered.

We have speculative calculations that suggest electrochemical mechanisms can produce SP anomalies of great amplitude for some special conditions and assuming the Planck approximation holds. Polarities appear to be controlled by the curvature of the thermal and concentration profiles. Concave upward thermal profile generate positive anomalies whereas concave upward concentration profiles generate negative anomalies. Concave downward concentration profile have characteristic small negative closures bounding a larger, central positive anomaly.

The derived equations can be used to interpret many features of field surveys if sufficient information on groundwater compositional variations exists. While this is not usually the case, the above results suggest electrochemical mechanisms should be included in any conceptual interpretation.

ACKNOWLEDGEMENTS

We would like to thank UNOCAL Geothermal for their permission to publish the Long Valley validation exercise. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory for contract number W-7405-ENG-48.

REFERENCES

- Aguilella, V.M., Mafe, S. and Pellicer, J., 1987, On the nature of the diffusion potential derived from Nernst-Planck flux equations by using the electroneutrality assumption: *Electrochim. Acta*, **32**, 483-488.
- Ahmad, M. U., 1964, A laboratory study of streaming potentials: *Geophys. Prosp.*, **12**, 49-64.
- Anderson, D. E. and Graf, D. L., 1978, Ionic diffusion in naturally-occurring aqueous solutions: use of activity coefficients in transition-state models: *Geochim. et Cosmo. Acta*, **42**, 251-262.
- Anderson, L. A. and Johnson, G. R., 1976, Application of the self-potential method to geothermal exploration in Long Valley, California: *J. Geophys. Res.*, **81**, 1527-1532.
- Bockris, J. O. and Reddy, A. K. N., 1973, *Modern electrochemistry*: Plenum Press.
- Bogoslovsky, V. V. and Ogilvy, A. A., 1973, Deformations of natural electric fields near drainage structures: *Geophys. Prosp.*, **21**, 716-723.
- Corwin, R. F., DeMouly, G. T., Harding, R. S. and Morrison, H. F., 1981, Interpretation of self-potential survey results from the East Mesa Geothermal Field, California: *J. Geophys. Res.*, **86**, 1841-1848.
- Corwin, R. F. and Hoover, D. B., 1979, The self-potential method in geothermal exploration: *Geophysics*, **44**, 226-245.

- Corwin, R. F. and Morrison, H. F., 1977, Self-potential variations preceding earthquakes in Central California: *Geophys. Res. Lett.*, **4**, 171-174.
- de Groot, S. R. and Mazur, P., 1984, *Nonequilibrium thermodynamics*: Dover Publ. Inc.
- Dorfman, M.H., Oskay, M.M. and Gaddis, M.P., 1977, Self-potential profiling- a new technique for determination of heat movement in a thermal oil recovery flood: SPE paper 6790 presented at 52nd Annual Conference of Soc. Petr. Eng., Am. Inst. Min., Metall. Petr. Eng., 1977.
- Ellis, A. J. and Mahon, W. A. J., 1977, *Chemistry and geothermal systems*: Academic Press Inc.
- Fitterman, D. V., 1978, Electrokinetic and magnetic anomalies associated with dilatant regions in a layered earth: *J. Geophys. Res.*, **83**, 5923-5928.
- _____ 1979, Calculations of self-potential anomalies near vertical contacts: *Geophysics*, **44**, 195-205.
- _____ 1983, Modeling of self-potential anomalies near vertical dikes: *Geophysics*, **48**, 171-180.
- Fitterman, D. V. and Corwin, R. F., 1982, Inversion of self-potential data from the Cerro Prieto geothermal field, Mexico: *Geophysics*, **47**, 938-945.
- Fitts, D. D., 1962, *Nonequilibrium thermodynamics*: McGraw-Hill Book Co. (Div. of McGraw-Hill, Inc.).
- Gay, S. P., 1967, A 1,800 millivolt self-potential anomaly near Hualgayoc, Peru: *Geophys. Prosp.*, **15**, 236-245.
- Hafemann, D.R., 1965, Charge separation in liquid junctions: *J. Phys. Chem.*, **69**, 4226-4231.
- Hearst, J. R. and Nelson, P. H., 1985, *Well logging for physical properties*: McGraw-Hill Book Co. (Div. of McGraw-Hill, Inc.).
- Helgeson, H. C., Kirkham, D. H. and Flowers, G. C., 1981, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5kbar: *Am. J. Sci.*, **281**, 1249-1516.
- Ishido, T., Kikuchi, T. and Sugihara, M., 1987, The electrokinetic mechanism of hydrothermal-circulation-related and production-induced self-potentials: Twelfth Stanford Workshop on Geothermal Reservoir Engineering.
- Ishido, T. and Mizutani, H., 1981, Experimental and theoretical basis of electrokinetic phenomena in rock-water systems and its application to geophysics: *J. Geophys. Res.*, **86**, 1763-1775.
- Kilty, K. T., 1984, On the origin and interpretation of self-potential anomalies: *Geophys. Prosp.*, **32**, 51-62.
- Kruger, F. C. and Lacy, W. C., 1949, Geological explanation of geophysical anomalies near Cerro de Pasco, Peru: *Econ. Geol.*, **44**, 485-491.
- Leckey, J.H. and Horne, F.H., 1981, Time-dependent cell potential and single-ion activity coefficients for a concentration cell with liquid junction: *J. Phys. Chem.*, **85**, 2504-2511.
- Lewis, R. E., 1974, Data on wells, springs and thermal springs in Long Valley, Mono County, California: U. S. G. S. open-file report.
- MacGillivray, A.D., 1968, Nernst-Planck Equations and the electroneutrality and Donnan equilibrium assumptions: *J. Chem. Phys.*, **48**, 2903-2907.
- Mafe, S., Pellicer, J. and Aguilera, V.M., 1986, Ionic transport and space charge density in electrolyte solutions as described by Nernst-Planck and Poisson equations: *J. Phys. Chem.*, **90**, 6045-6050.

- Mafe, S., Pellicer, J., Aguilera, V.M. and Garrido, J., 1987, A study of the electroneutrality assumption in the vicinity of the inner membrane boundaries: *J. Non-Equil. Thermodyn.*, **12**, 161-168.
- Mariner, R. H. and Willey, L. M., 1976, Geochemistry of thermal waters in Long Valley, Mono County, California: *J. Geophys. Res.*, **81**, 792-800.
- Miller, D. G., 1966, Application of irreversible thermodynamics to electrolyte solutions. I. determination of ionic transport coefficients l_{ij} for isothermal vector transport processes in binary electrolyte systems: *J. Phys. Chem.*, **70**, 2639-2659.
- _____ 1967a, Application of irreversible thermodynamics to electrolyte solutions. II. determination of ionic transport coefficients l_{ij} for isothermal vector transport processes in ternary electrolyte systems: *J. Phys. Chem.*, **71**, 616-632.
- _____ 1967b, Application of irreversible thermodynamics to electrolyte solutions. III determination of ionic transport coefficients l_{ij} for isothermal vector transport processes in n-component systems: *J. Phys. Chem.*, **70**, 2639-2659.
- Nigrini, A., 1970, Diffusion in rock alteration systems: I. prediction of limiting equivalent ionic conductances at elevated temperatures: *Am J Sci.*, **269**, 65-91.
- Nourbehecht, B., 1963, Irreversible thermodynamic effects in inhomogeneous media and their applications in certain geoelectrical problems: Ph. D. dissertation, M.I.T.
- Ogilvy, A. A., Ayed, M. A. and Bogoslovsky, V. A., 1969, Geophysical studies of water leakages from reservoirs: *Geophys. Prosp.*, **22**, 36-62.
- Robinson, R. A. and Stokes, R. H., 1959, *Electrolyte solutions*: Butterworth and Co. Publ.
- Sato, M. and Mooney, H. M., 1960, The electrochemical mechanism of sulfide self-potentials: *Geophysics*, **25**, 226-249.
- Shaw, D. J., 1980, *Introduction to Colloid and Surface Chemistry*: Butterworth and Co. Publ.
- Sill, W. R., 1983, Self-potential modeling from primary flows: *Geophysics*, **48**, 76-86.
- Sorey, M. L. and Lewis, R. E., 1976, Convective heat flow from hot springs in the Long Valley caldera, Mono County, California: *J. Geophys. Res.*, **81**, 785-791.
- Telford, W. M., Geldart, L. P., Sheriff, R. E. and Keys, D. A., 1976, *Applied Geophysics*: Cambridge Univ. Press.
- Tuman, V. S., 1963, Thermo-telluric currents generated by an underground explosion and other geological phenomena: *Geophysics*, **28**, 91-98.
- Wendt, R. P., 1965, The estimation of diffusion coefficients for ternary systems of strong and weak electrolytes: *J. Phys. Chem.*, **69**, 1227-1237.
- White, D. E., Muffler, L. J. P. and Truesdell, A. H., 1971, Vapor-dominated hydrothermal systems compared with hot-water systems: *Econ. Geol.*, **66**, 75-97.
- Willey, L. J., O'Neill, J. R. and Rapp, J. B., 1976, Chemistry of thermal waters in Long Valley, Mono County, California: U. S. G. S. open-file report.
- Zablocki, C. J., 1975, Mapping thermal anomalies on an active volcano by the self-potential method, Kilauea, Hawaii: Proc. Second Annual U. N. Symposium on the Devel. and Use of Geothermal Resources, San Francisco, **2**, 1299-1309.

Zohdy, A. A. R., Anderson, L. A. and Muffler, L. J. P., 1973, Resistivity, self-potential, and induced-polarization surveys of a vapor-dominated geothermal system: *Geophysics*, **38**, 1130-1144.