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A CRITICAL EXAMINATION OF THE CONDITION OF  
ELECTRONEUTRALITY IN GROUNDWATER

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## A CRITICAL EXAMINATION OF THE CONDITION OF ELECTRONEUTRALITY IN GROUNDWATER

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### ABSTRACT

The evaluation of overall analytical accuracy of groundwater chemistry is often made through the electroneutrality equation, which requires the equivalents of cations in a unit mass or volume of solution equal those of anions. This implies that electroneutrality is a characteristic property of groundwater. There are a number of arguments for the existence of electroneutrality, such as widespread reports of electroneutrality (within analytical accuracy) and the valid application of reversible thermodynamics, as well as arguments against it, such as sorption, ion exchange, and radioactive decay. By presenting these arguments and by examining the current views in hydrogeology on the definition of systems and on scales of examination, this paper leads to the conclusion that electroneutrality is not a theoretical *a priori* condition of groundwater, but is a commonly observed condition within analytical accuracy.

Author's Note: Through peer review, I have been told that the condition of electroneutrality is not open to discussion because it is a fundamental chemical property. However, a discrepancy in the geologic literature apparently exists and indicates either (1) electroneutrality is not a fundamental property in an open system, (2) a number of hydrogeologic theories are not soundly developed, or (3) the concepts of scale and system which are better defined for physical hydrogeology require further refinement for chemical hydrogeology. The latter explanation appears to explain best the problem. Because of page limitations, a peer review of this paper and my response covering several detailed issues cannot be included here but are available upon request.

### 1. INTRODUCTION

In the realm of ion-pairing theory, dissolved solids in groundwater possess both chemical and electrical properties. An integrated chemoelectrical view of cations and anions leads to a commonly employed equation for evaluating the overall accuracy of cation-anion analyses, the electroneutrality equation. One form of the equation is:

$$\text{ERROR} = [(\text{CAT}-\text{AN})/(\text{CAT}+\text{AN})] \times 100\% \quad (1)$$

where CAT = sum of all cations in milliequivalents/liter  
AN = sum of all anions in milliequivalents/liter

Milliequivalents are obtained by multiplying the number of millimoles per liter of each ion by the absolute value of each species' ionic charge. The "ERROR" in Equation 1 implies the water sample is theoretically electroneutral or "charge balanced".

It is surprising how rigidly this equation is employed in light of the wide acceptance of the non-ideal, scale-dependent, stochastic natures of other hydrogeologic concepts such as hydraulic conductivity, dispersion, and diffusion. Additionally, a higher or lower ERROR will be obtained from a speciated water analysis relative to the unspicated water analysis. In order to question the concept of charge balance in groundwater, this paper examines arguments for and against the expectation of electroneutrality. Because the validity of the arguments are sensitive to the scale and to the definition of a hydrogeologic system, an initial discussion of scale and system will be presented and later expanded in the arguments.

### 2. SCALE DEPENDENCY AND DEFINITION OF SYSTEM

Ions are extremely small entities (approximately  $6 \times 10^{20}$ /millimole) and a liter of water contains roughly  $3 \times 10^{25}$  molecules of  $\text{H}_2\text{O}$  and ions. If one ion is isolated in an imaginary closed box, thereby defining a closed system, then electroneutrality does not exist in the system. If the system is expanded to include 1 milliliter of solution (water and ions), there is apparently no theoretical *a priori* reason for electroneutrality to exist in the system. Perhaps 10 liters, for example, must be taken as the system in order to assure the existence of bulk electroneutrality. A further discussion of this point through statistical mechanics, which is the basis of thermodynamics, is presented in a later section. At this point, the preceding discussion leads to two important complications.

The first complication is that the "scale of examination" may not coincide with the scale of the system. An example can best explain the distinction (Baveye and Sposito, 1984, and Cushman, 1986, provide a mathematical discussion). If 100 liters of groundwater solution is required to attain bulk electroneutrality and this 100 liters is defined as a closed system, then the removal of a 1 L sample for analysis may not provide an electroneutral sample. In this example, the scale of examination (the 1 liter sample) does not coincide with the scale of the electroneutral system. In some cases, the scale of examination is assumed to define the scale of the system.

The second and more formidable complication is the valid definition of a hydrogeologic system where the mobile aqueous phase is in intimate contact with a relatively stationary porous solid phase. In pure geochemistry, a system can simply be defined as a quantity of solid and its associated porewater. In chemical hydrogeology, if a system is defined on the basis of a quantity of solid, then groundwater of changing chemical composition on some time scale is constantly entering, interacting with, and leaving the system. On the other hand, if a hydrogeologic system is defined on the basis of a quantity of groundwater solution, then the porous solid phase of changing chemical composition (microstrata to formations) is constantly entering, interacting with, and leaving the system. In other words, pure geochemistry provides a closed system of immobile phases whereas hydrogeology can only provide open system (e.g., Marle, 1982) that is affected by outside processes which move through the system and allow the accumulation/loss of matter and energy in the system. It is the open systems that could allow the accumulation of charge imbalance, as explained in the following section.

Through these concepts of scale and system, the arguments for and against electroneutrality in groundwater can now be presented. The arguments against electroneutrality are presented first through theoretical and applied cases, which draw on many areas of geology such as geochemistry, borehole geophysics, and radioactive decay, although some of the arguments allow only a negligible charge imbalance (Section 3.5).

### 3. ARGUMENTS AGAINST ELECTRONEUTRALITY

#### 3.1 Mechanism Of Mineral Precipitation-Dissolution

Although an ideal crystal of a mineral may have no net electrical imbalance, real crystals (and amorphous minerals) can have a net charge because of crystal imperfections, isomorphous substitution in the crystal structure, and irregular, broken surfaces. An electrical charge at the surface is detectable and accounts for the geochemical reactions of sorption and ion exchange (Section 3.2). Upon dissolution of a crystal(s), an originally electroneutral, undersaturated solution will take on the net charge of the crystal(s).

During precipitation from an electroneutral groundwater solution, a crystal can develop lattice imperfections and incorporate foreign ions from solution through co-precipitation. As well, crystals grow not through occasional additions of entire electroneutral sheets onto the surface, but through continuous spiral or irregular planes. In these ways, an electrically unbalanced crystal can develop. Correspondingly, any charge imbalance in the crystal results in an equal, but oppositely charged, imbalance in the solution. An observation can be made here that the combination of the liquid and solid phases at this point represents an electroneutral system, but this observation is of little hydrogeologic relevance for two reasons. First, in hydrogeology, the aqueous phase is analyzed either independent of or excluding the solid phase, thereby leading to the requirement of a unbalanced aqueous analysis. Second, the charged groundwater will flow away from the equally, but oppositely, charged solids. The magnitude of the imbalance would depend on many

conditions and is discussed in detail in Section 3.5.

In the more realistic open systems of one mobile phase, charge imbalances could accumulate with flow. One can envision many related scenarios such as where an initially electroneutral groundwater precipitates an unbalanced mineral in a stratum before passing into other strata. Afterwards, an undersaturated, electroneutral groundwater flows into the mineralized stratum and dissolves the mineral. In this way, the total accumulated charge imbalance in the precipitating groundwater mass, which is now downgradient, will be equal to, but opposite in charge of, the dissolving groundwater mass.

#### 3.2 Mechanism Of Sorption and Ion Exchange

When a relatively stable mineral, quartz for example, is ground into smaller grains and these grains are added to a pH-neutral water with dissolved solids (closed system), some cations will commonly be drawn to and tightly bound to the negatively charged surface. If the bound cations do not completely neutralize the surface charge, a "diffuse zone" of more loosely held cations (with some anions drawn by the concentrated cations) and polar water molecules will lie near the surface. The strength with which cations in the diffuse zone are held near the surface decreases from the inner boundary to the outer boundary. The outer boundary extends theoretically to infinity, but practically has a limit because ions are discrete parcels of mass and charge. The combined surface/diffuse-zone region can claim electroneutrality, but by necessity creates a net negative charge in the free (unbound) groundwater. Alternatively, one can say that the solid and its surface remains charged while the total water phase including the tightly bound cations remains electroneutral. The most realistic scenario for flowing groundwater probably lies between these two alternatives and is discussed below.

It is interesting to note that essentially all current work on sorption (and exchange) reactions calls for electroneutrality when the crystal surface, bound ions, and diffuse zone are taken as a system (e.g., James and Parks, 1982) while the resulting, unbalanced bulk water is ignored. On the other hand, essentially all current work on aqueous reactions implies electroneutrality in the water. When these two areas of research are combined, as is often required for hydrogeology, there arises two questions: (1) where is the boundary between the solid and liquid phases and (2) which phase, if any, can claim electroneutrality. These questions will be addressed as clarifying details are presented.

The simple scenario of adsorption presented above is not representative of most groundwater systems, in which the grain surfaces have been in contact with water for long periods of time. In most cases, bound ions and diffuse zones have previously accumulated and can only be modified by ion exchange. Through ion exchange with established surfaces, aqueous cations are traded for the adsorbed cations, and surface exchange sites may concurrently release  $H^+$  or  $OH^-$  or undergo other alterations to retain reaction electroneutrality. As long as the exchange reaction maintains an equal exchange of charge to and from each phase, the net charge (zero, for example) for each phase remains constant. However, there are apparently some exchange reactions (e.g. Cases 2 and 8 in Table 1 of Sposito (1983)) which transfer some charge from one phase to the other

similar to adsorption reactions, resulting in varying imbalances in each phase. These reactions are referred to as "unbalanced exchange reactions" in this paper.

The examination of these unbalanced ion-exchange and adsorption reactions on the level where the bulk water and solid matrix are taken as one system may initially cause little concern because the combined groundwater and solid matrix apparently still retain the same net charge. In the open systems of hydrogeology, though, groundwater flow carries the groundwater away from the exchange sites and, thus, one or both separated phases can carry a net charge. Therefore, in answer to the aforementioned question of which phase can claim electroneutrality, the answer is neither phase is necessarily electroneutral when the unbalanced ion-exchange reactions operate, no matter where the boundary between the solid and liquid phases is located. The answer for occasions when electrically balanced ion exchange occurs or no exchange/sorption reactions operate first requires a closer look at the diffuse zone.

The bound ions on a crystal surface can be thought of as part of the crystal because of the strong bonds with the exchange sites, although the binding can alternatively be viewed as a continuum with the diffuse zone. In any case, the diffuse zone is more of an electrostatic effect, where the strength of attraction decreases with distance from the surface. The outer portion of the diffuse zone will be swept away (sheared) as groundwater flows (e.g. Nielsen et al., 1986). The width of zone that is swept away depends on the energy expended by the groundwater; for example, the greater the velocity, the greater the width of the diffuse zone that is sheared away. Consequently, the practical boundary between the mobile aqueous phase and the relatively immobile solid phase lies somewhere in the diffuse zone and likely is dependent on the velocity of the water and the charge density of the surface. By employing this reasoning, it appears that electroneutral groundwater probably remains electroneutral if velocity remains constant through an area of sheared diffuse zones while at the same time the region of solid surfaces and immobile sheared diffuse zone essentially remains electrically charged because of incompleteness. On the other hand, if velocity decreases or increases in a transient system, charge imbalance could develop in the groundwater and could decrease or increase, respectively, in the surface/diffuse-zone region. This effect can occur in response to both natural transient disturbances and artificial disturbances such as pump tests and groundwater sampling. Possible magnitudes of imbalances are addressed in Section 3.5.

### 3.3 Mechanisms Of Diffusion and Dispersion

In diffusion-dominated situations, non-equilibrium conditions prevail (Kubo, 1986) and charge imbalances can develop because the diffusion coefficient for each ionic species is slightly different. Thus, in low-permeability strata, charge imbalances could develop over long periods of time. On the other hand, in dispersion-dominated situations, charge imbalances cannot develop in a similar fashion as diffusion because current theory attributes dispersion to velocity and dispersivity, independent of the unique behavior of different ionic species. It is intriguing to consider species-dependent dispersion; however, this would only add to the presently precarious situation (Sposito et al., 1986).

Because dispersion represents a gradual mixing of two or more masses of water, a deterministic view of dispersion indicates an electroneutral water would result from the mixing of two electroneutral water or, by chance, from the mixing two water masses of exactly opposite imbalances. In addition, the mixing of an unbalanced water and an electroneutral water would result in an unbalanced water closer to electroneutrality.

### 3.4 Mechanism Of Radioactive Decay

As an atom progressively decays through a decay series, its chemical properties including valence vary. For example, the upper portion of the  $^{238}\text{U}$  decay series indicates the following transitions for a  $^{238}\text{U}$  atom:  $^{238}\text{U}^{4+,5+, \text{ or } 6+} \rightarrow ^{234}\text{Th}^{4+} \rightarrow ^{234}\text{Pa}^{5+} \rightarrow ^{234}\text{U}^{4+,5+, \text{ or } 6+} \rightarrow ^{230}\text{Th}^{4+} \rightarrow ^{226}\text{Ra}^{2+}$ . Because of this variation, an electroneutral system containing only  $^{230}\text{Th}^{4+}$  and  $\text{SO}_4^{2-}$  in a 1:2 millimolar ratio, for example, will eventually contain  $^{226}\text{Ra}^{2+}$  and other daughter products and  $\text{SO}_4^{2-}$  in a 1:2 millimolar ratio. Furthermore, radioactive decay in effect creates "new" matter from a geochemical viewpoint by ejecting alpha particles, which are essentially helium nuclei without shell electrons, and beta particles, which are essentially electrons. The alpha particles can become the helium atoms often found in radioactive areas by capturing electrons from shells of other ions, i.e. by increasing ion valence towards more positive values, and the beta particles can lower the valence of ions towards more negative values upon shell capture. In these ways, a charge imbalance can accrue in a radioactive hydrogeologic system.

### 3.5 Possible Magnitudes Of Imbalance Developed By The Aforementioned Mechanisms

Before proceeding to published mechanisms for charge imbalances, it is instructive at this point to examine the magnitude of imbalance that mineral precipitation-dissolution, sorption and ion exchange, diffusion, and radioactive decay can produce.

For simple illustrative purposes, the magnitude of charge imbalance in a mineral undergoing precipitation-dissolution (Section 3.1) is roughly approximated by the Cation Exchange Capacity (CEC) of the mineral although it is clear that crystallographic features such as coordination and outside variations such as in aqueous pH can modify the CEC value and that deep internal crystal imbalances make a relatively minor contribution to CEC. CEC values in groundwater generally vary from approximately 0.1 to 100 milliequivalents/100 g of mineral, suggesting that charge imbalances of approximately  $10^{-3}$  to 1 milliequivalent/liter could develop upon precipitation-dissolution of a moderately soluble mineral (about 1 g/L or roughly 1-10 millimoles/L). The precise degree of imbalance will depend on such factors as the solubility, ratio of crystal surface to volume (grain vs. grain coating), solution composition, ionic strength, and reaction kinetics. In any case, the ability to practically detect this imbalance through a water analysis and Equation 1 depends on the total number of milliequivalents/L in solution. For a moderate groundwater with several milliequivalents/L, the charge imbalance will be less than analytical accuracy and, thus, not detectable.

The general magnitude of any charge imbalance resulting from sorption or ion exchange can be inferred from the scenario developed in Section 3.2. For the groundwater mass which first contacts a fresh surface (simple

adsorption), the aqueous imbalance will reflect the CEC as a maximum limit. In a stratum with a porosity of 0.40 and a matrix density of 2.7, 1 liter of groundwater will be in contact with 4050 g of matrix. With a generally observed CEC range of 0.1 to 100 meq/100 g, an imbalance of 4.05 to 4050 meq/L could occur. Obviously, the higher imbalances cannot develop in 1 liter of most groundwaters because of lack of sufficient dissolved solids (4050 meq/L). However, the higher imbalances suggest that, alternatively, many liters of groundwater could be affected by only 100 g of matrix. Even a low CEC material could conceivably cause a significant accumulation of charge imbalance with time, because one liter of fast-moving groundwater through the low CEC material could accumulate a similar degree of imbalance in a unit of time as slow-moving groundwater through high CEC material.

For groundwater masses subjected to unbalanced ion exchange reactions, the imbalance can at most be equivalent to the above sorption values. For groundwater undergoing balanced exchange or no liquid-solid interaction, the water will maintain its original charge if velocity remains constant. If velocity decreases at a location, a net negative imbalance may develop by net loss of cations to the incomplete diffuse zone, but this loss will be negligible compared to the CEC-based values.

For diffusion (Section 3.3), the possible magnitude of imbalance is dependent on the difference between individual diffusion coefficients, the original concentrations, and the length of time of diffusive movement. Thus, the maximum magnitude is theoretically high. Similarly, the possible range of imbalance caused by radioactive decay (Section 3.4) is dependent on original concentrations, length of time for decay relative to radionuclide half-lives, and the sequence of elements formed.

Charge imbalance as developed in the previous sections is caused by the relationship of mass and energy in ionic dissolved solids. If a charge imbalance develops in an electroneutral water, energy must be expended and, thus, the imbalance represents potential energy which is available to do work. Therefore, a charge imbalance in groundwater represents a potential that must be considered when evaluating all other potentials (e.g. gravity, pressure, chemical, osmotic) to define groundwater movement and chemistry. This will be discussed further in Section 5.

### 3.6 Published Reports Of Processes Leading To Aqueous Charge Imbalance

The previous sections have discussed through theory the common reactions that can lead to charge imbalances in groundwater, although experimental evidence for the imbalance in groundwater through those reactions is generally lacking. However, evidence of imbalances is reported (often indirectly) for more dramatic situations, especially ion filtration in highly compacted clays and clay-rich strata, artificial desalination, specific conductance measurements, and SP borehole logs.

When clay is highly compacted, the positively charged diffuse zones on opposite surfaces of a pore are close to, or achieve, overlapping. This results in chemo-electrical effects where (1) the positively charged diffuse zones electrically repel cations attempting to flow past them and (2) the diffuse zones attract aqueous anions (e.g. Kharaka and Berry, 1973; Bresler, 1973; Bresler and Laufer, 1974). These differential attractions and repulsions, which can be grouped under "ion filtration", can result in

a charge imbalance in groundwater (e.g. Elrick et al., 1976).

In a suspension (water and suspended charged particles), the electrical charge of the particles is known to disrupt electrically based measurements such as pH (e.g. Linnet, 1970). A suspension presents an interesting deviation from Section 3.2 in that the charged surfaces are part of and in motion with the groundwater and, thus, the suspension is charge-unbalanced no matter where the boundary is drawn between the liquid and diffuse layer. An argument can be made that the definition of "groundwater" does not include suspended particles (the definitions in NWWA, 1985, do not include any chemical parameters); however, if the suspension is filtered, the discussion in Section 3.2 on sheared diffuse layers then applies. An interesting discussion of the suspension effect (also known as the Donnan potential) can be found in Overbeek (1953), where ion partitioning and ion mobilities between the water and the suspended particles are discussed and where techniques that are probably applicable for the measurement of any charge imbalance are briefly reviewed.

Common desalination techniques such as electrodialysis (e.g. Buros, 1985) create chemo-electrically unbalanced water by the use of charged electrodes and membranes to separate anions and cations. Furthermore, the elimination of the membrane essentially results in a cell for the measurement of specific conductance in water. For groundwater conductance measurements, the conductance cell causes cations to move towards one electrode and anions to the other. The bulk water remains electroneutral, but two unbalanced waters exist if the sample is arbitrarily divided into two portions around each electrode. Some conductance meters continuously reverse the polarity of the electrodes so that an extreme, disrupting aqueous charge does not accumulate near the electrodes.

SP borehole logs are apparently dependent on charge imbalances to produce deflections at lithologic contacts (e.g. Schlumberger Ltd., 1972). The ion-filtration capacity of shales reportedly allow only the movement of cations to the borehole, resulting in charge imbalances across a "membrane" which in turn produces a "membrane potential" (Schlumberger Ltd.). This scenario is apparently synonymous with electrical osmosis, which is reportedly minor (Graf, 1982).

A detailed laboratory study of chemo-electrical behavior of ions in groundwater has been recently reported (Runnels and Larson, 1986). In this study, platinum electrodes were placed at both ends of a column containing quartz-feldspar sand and  $\text{CuSO}_4$  solution. When a voltage between 1.5 and 2.5 V DC was imposed on the electrodes, the  $\text{Cu}^{2+}$  migrated towards the negatively charged cathode and was electrochemically reduced onto the platinum while  $\text{SO}_4^{2-}$  migrated towards the anode. At the cathode, a cation excess of about 7% of total cations and anions (approximately 0.9 milliequivalents/L) was observed and attributed to analytical error in order to maintain electroneutrality. In other sections of the column, including the region near the anode, charge imbalance was often less than 1%. However, in this region near the anode, because of the strong applied voltage, water was apparently being oxidized to  $\text{H}^+$  (which must then be repelled from the anode) and  $\text{O}_2$  gas. The  $\text{H}^+$  could provide the needed cations to obtain near electroneutrality. Because this concept of electromigration of ions and contaminants in groundwater is gaining

attention for contamination mitigation (Runnels and Larson) and for geochemical exploration (Shmakin, 1985), future studies may provide more knowledge on the development of charge imbalance in groundwater.

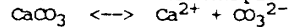
#### 4. ARGUMENTS FOR ELECTRONEUTRALITY

##### 4.1 Reported In-Field Studies

The most potent argument for the existence of electroneutrality in groundwater is the general lack of reported imbalances in field studies. Part of this deficiency may be the result of hydrogeologists returning unbalanced analyses to an analytical laboratory with a request for a balanced analysis and the result of the belief that an unbalanced analysis indicates at least one significant ion was not measured. Of course, these may be valid practices in many cases and, in any event, they probably cannot account for the widespread reporting of balanced analyses. Because Section 3.5 indicates that charge imbalance can be below the level of analytical accuracy, charge imbalance may exist but could often be undetectable. Nevertheless, this argument for electroneutrality based on widespread evaluation cannot be ignored.

##### 4.2 Reversible Thermodynamics

In hydrogeology, dissolved solids are treated as ionic particles. This treatment of ionization is outside the realm of thermodynamics, but can be linked to reversible thermodynamics through assumptions on ion formation from "chemical components" (e.g. Chapter 7 of Nordstrom and Munoz, 1985) and on single-ion activity coefficients from a component activity coefficient. As an example of ion formation from a component:



where  $\text{CaCO}_3$  represents neither a neutral-charge aqueous complex nor a mineral. Similarly, an aqueous solution of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Al}^{3+}$  can be thermodynamically defined as a  $\text{CaO-H}_2\text{SO}_4\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$  system. These components show that electroneutrality is not an assumption, but an implicit rule, of thermodynamics.

Therefore, for thermodynamics to be applied to a system, the system must be electroneutral. It is possible that the opposite reasoning may be occasionally used in hydrogeology: because thermodynamics can often validly describe groundwater geochemistry, the system must be electroneutral. This opposite reasoning is unacceptable because a minor charge imbalance will not likely be sufficient to render thermodynamics inapplicable.

Other than the preceding empirical argument for electroneutrality (Section 4.1), thermodynamics provides the only other strong argument for charge balance in groundwater. If this thermodynamic argument is ignored, then all other arguments lead to the general conclusion: charge imbalance is within overall analytical accuracy under relatively normal conditions but can become significant under unusual conditions. Therefore, the rigid application of Equation 1 in hydrogeology may be simply the result of the common use of thermodynamics. Because of this possibility, it is worthwhile to examine in detail some fundamental concepts of thermodynamics by returning to the discussion of scale and system initiated in Section 2.

#### 5. A POSSIBLE RESOLUTION OF ARGUMENTS FOR AND AGAINST ELECTRONEUTRALITY

The search for the Representative Elementary Volume (REV) in physical hydrogeology is relevant to this study and is used here in its simple conceptual form and not as a rigorous concept (Baveye and Sposito, 1984; Berkowitz and Bensabat, 1985; Baveye and Sposito, 1985). As a volume under consideration increases from zero, the value of some parameter such as porosity initially fluctuates then reaches a steady average value (at the REV), and then the value again fluctuates as the volume increases further. The search for an REV for electroneutrality can start with the description of systems in Section 2 of either a stationary volume of porous solids with groundwater passing through it or a stationary volume of groundwater with passing porous solids. The former system will be used for the following discussion.

Based on Section 3.1, an initially electroneutral groundwater is assumed to precipitate non-ideal unbalanced crystals and, thus, the groundwater becomes equally but oppositely charged and moves downgradient. The succeeding electroneutral groundwater then dissolves some of the unbalanced crystals and takes on their charge. In this example, the REV for electroneutrality could be defined as the combination of the downgradient water, the upgradient water, and the upgradient solids; however, the downgradient water is in contact with solids that may be changing its imbalance through any of the processes in Section 3 and these downgradient solids were possibly influenced by the groundwater located even further downgradient. The REV for electroneutrality therefore eventually expands to encompass an entire formation, and entire basin, the earth, and the universe. While this may sound ludicrous, an REV consisting of the universe is not foreign to some aspects of physics and chemistry. Bohm (1951), as quoted by Ziemelis (1986), concludes "the entire universe must, on a very accurate level, be regarded as a single indivisible unit in which separate parts appear as idealizations permissible only on a classical level of accuracy of description". More relevant to this discussion, statistical mechanics, which provides bulk descriptions of systems with an enormous number of particles and is the basis of thermodynamics (e.g. Balescu, 1975), requires the universe as a system for the unquestionably valid application of thermodynamics (the "thermodynamic limit", e.g. Section 4.7 of Balescu). Thermodynamics is not necessarily applicable to any system smaller than the universe unless certain conditions on equivalence are met. In other words, the free-energy of a system smaller than the universe may not be equal to the free-energy predicted by thermodynamics. This point will be discussed further below.

Another important aspect in the definition of a system for the valid application of statistical mechanics is that any system smaller than the universe must have a "negligible" volume of boundary layer, in which conditions vary from those of the system's bulk volume. If the boundary layer is significant, then statistical mechanics and thermodynamics may not be applicable to the system. Geochemists observe this point when the solubility of a crystal increases as the volume of the crystal decreases; for example, Iler (1979) explains the increasing solubility of amorphous silica at grain diameters less than 10 nanometers. Because groundwater passes through a porous solid phase, a hydrogeologic system can have a

relatively large boundary layer.

The previous two paragraphs indicate that thermodynamics may not necessarily predict the chemical energy in a system smaller than the universe. This situation is rendered more complex, but not unsolvable, when energy transformations are allowed in the system. For example, the potential energy of groundwater represented by gravity (elevation potential) is linked to the groundwater's chemical potential energy (e.g. Section 7.6 of Sposito, 1981) and a change in one potential can affect the other potential (see also Olsen, 1985). As a second example, a difference in salinities (chemical potential) across a membrane produces chemical osmotic pressure which can overcome some degree of a reverse pressure-potential gradient. Another example is presented in Section 3.2 where variations in kinetic energy of flow can be theoretically converted to charge imbalance through sheared diffuse layers. These examples provide further argument for the integrated examination of physical and chemical aspects of hydrogeology: "Physical and chemical hydrogeology should not be separated since the interaction between physical and chemical parameters can no longer be ignored" (Discussion Session No. 8, First Canadian/American Conference on Hydrogeology, p.321 of Hitchon and Wallick, 1984). There have been initial steps in the direction of linking various forms of energy in groundwater (e.g. Marle, 1982), but until more work is done it is difficult to predict the impact of energy transformations on the application of thermodynamics in hydrogeology.

Therefore, thermodynamics and the accompanying requirement of electroneutrality are not necessarily applicable to groundwater based on the conditions required for a valid system and on the theoretical and observed mechanisms against electroneutrality in Section 3. However, the widespread observation of near electroneutrality within analytical accuracy indicates that groundwater (the aqueous phase) often does meet the system requirements for thermodynamics and electroneutrality on the current scales of examination. The current sampling scales from piezometers and monitor wells are often in the range of several milliliters to several liters and the scales of laboratory chemical analysis are in the range of fractions of milliliters to hundreds of milliliters. Despite the scale of examination, this paper has presented sufficient arguments to justify a more cautious use of Equation 1 in hydrogeologic studies.

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