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This volume was originated by the Mineral Processing Division of the Society of Mining Engineers of AIME, as a memorial to the late Dr. A. M. Gaudin, inspiring educator and distinguished engineer.

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Chapter 4

ANALYSIS OF THE SURFACE POTENTIAL DEVELOPED
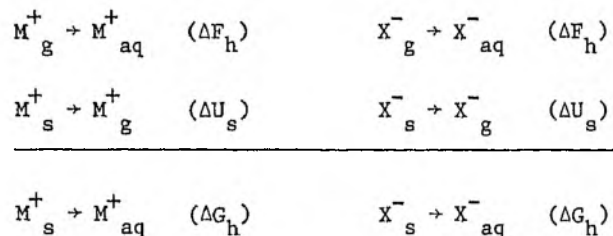BY NON-REACTIVE IONIC SOLIDS

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ABSTRACT

The sign of the surface potential for complex non-reactive ionic solids cannot be predicted solely from consideration of the hydration energy of gaseous ions which constitute the ionic lattice. Accurate analysis of these systems must involve the hydration energy of surface ions, which requires knowledge of the crystal structure, the identification of cleavage planes, and the calculation of binding energies of surface ions. Surface binding energies for ionic solids can be determined if the Surface Madelung Constant is known.

A computational technique was developed for the calculation of Madelung Constants for infinite lattices which gives excellent agreement with the values calculated by other more complicated methods reported in the literature. Extension of this technique permits the calculation of Surface Madelung Constants and binding energies of surface ions, ΔU_s, for semi-infinite solids. The hydration free energy of gaseous ions, ΔF_h, together with the calculated binding energy of surface ions, ΔU_s, allows calculation of the hydration energy of surface ions, ΔG_h, as for the case of the ionic solid, MX:

$$M^+_g \rightarrow M^+_{aq} \quad (\Delta F_h) \qquad X^-_g \rightarrow X^-_{aq} \quad (\Delta F_h)$$

$$M^+_s \rightarrow M^+_g \quad (\Delta U_s) \qquad X^-_s \rightarrow X^-_g \quad (\Delta U_s)$$

$$\overline{\phantom{M^+_s \rightarrow M^+_{aq} \quad (\Delta G_h) \qquad X^-_s \rightarrow X^-_{aq} \quad (\Delta G_h)}}$$

$$M^+_s \rightarrow M^+_{aq} \quad (\Delta G_h) \qquad X^-_s \rightarrow X^-_{aq} \quad (\Delta G_h)$$

From the relative magnitudes of the ionic surface hydration energies, ΔG_h, the sign of the surface potential can be predicted for complex ionic solids. The analysis accounts for the fact that fluorite exhibits a positive surface potential in the absence of specific chemical interactions. Further, it is demonstrated why the sign of the surface potential for simple ionic solids can be predicted from the hydration energy of gaseous ions.

Ultimately, the analysis of the surface potential of non-reactive ionic solids in terms of ionic surface hydration energies may allow calculation of the point of zero charge for these solids. Preliminary calculations of the PZC are in error by orders of magnitude and from a quantitative standpoint the analysis needs further refinement.

INTRODUCTION

Interfacial Potential and Surface Charge

Potential difference across an interface develops from separation of charges. Although this is a fundamental fact, the detailed process by which charge separation is accomplished differs from system to system and even for a particular system there could be several mechanisms operative.

The potential across a liquid-liquid interface, called the distribution potential, was explained by Nernst (1) in 1892 to be the result of the difference in solubilities of the oppositely charged ions in the two phases. This is essentially the reasoning used by Beutner (2) to explain the electromotive force generated between a salicylic aldehyde solution in salicylic acid, and an aqueous KCl solution. Nernst's theory is the accepted explanation for the interfacial potential between two immiscible electrolytes. Any potential that is traceable to adsorbed monolayers at the interface is quickly cancelled by migration of ions across the interface.

The situation is generally more complicated for a solid-liquid system. Here the redistribution of ions by interfacial migration is generally kinetically hindered and in many cases only the liquid phase is electrolytic.

Quantitative description of the charge distribution in the liquid electrolyte is given by the well known double layer theory. However complete details regarding the origin of potential at the solid surface are lacking. Many mechanisms for the development of potential at the solid surface in aqueous systems have been proposed and can be classified as belonging to one of three categories; specific chemical interaction, lattice substitution, and hydration of lattice atoms.

Specific Chemical Interaction. Specific chemical interactions include reactions with the aqueous phase which lead to the formation of dif-

ferent surface compounds or surface species. One of the most common
mechanisms of charge generation, operative in many systems including
oxides, silicates, and semisoluble salts, is the formation and subse-
quent dissociation of surface acid groups. In the case of quartz,
SiO_2, many investigators (3,4,5) have explained its electrokinetic be-
havior in terms of this model. The surface silicic acid, or silanol
group, dissociates to release hydrogen ions to the solution, leaving
the surface with a negatively charged silicate group. The hydrogen
ion is said to be potential determining because the surface charge den-
sity and surface potential are determined by the bulk phase concentra-
tion of hydrogen ion.

In systems involving the pure solid, and in the absence of foreign,
polyvalent cations in solution, this mechanism is difficult to distin-
guish from that proposed by Parks and de Bruyn (6) where the surface
charge is attributed to the adsorption of hydroxy complexes. However,
in systems containing foreign, polyvalent cations at critical pH val-
ues, surface potential modulation is related to the adsorption of hy-
droxy complexes (7) and/or the nucleation and growth of colloidal hy-
droxide on the solid surface (8).

Although hydrogen ion adsorption is cited as one of the common ex-
amples of specific chemical interactions, chemisorption reactions or
surface oxidation-reduction reactions would be included in this cate-
gory. In most of these systems the surface charge density will be
determined by the reactant's concentration, the solid's surface ac-
tivity, and the extent of the chemisorption reaction.

Lattice Substitution. The second mechanism whereby the solid surface
may acquire a potential is the situation in which a charge imbalance
arises from lattice substitutions which result in the solid acquir-
ing a fixed surface charge density. The classic example for this me-
chanism is the clay-type minerals (9,10). The constant surface charge
density developed is compensated by interlayer ionic charges (exchange-
able cations) which are released when in contact with water to form the
counterions (11). Unlike the first mechanism, specific chemical in-
teraction, the surface charge on the interlayer surfaces is not deter-
mined by the concentration of exchangeable cations, but is constant.

Hydration of Lattice Ions. In the absence of specific chemical inter-
actions and charge deficiency due to lattice substitution, the poten-
tial a surface develops will be determined simply by preferential hy-
dration of surface atoms. In the case of an ionic solid, the ionic
constituents migrate to establish thermodynamic equilibrium between
the two phases (11). Grimley (12) notes that ionic migration must oc-
cur if the chemical potential for a given ion differs across the inter-
face. He verified the dynamic exchange of ions in the case of an AgBr-
aqueous solution by using radioactive Ag and Br as tracers. Further-
more, in 1943 Langer (13) indicated that the exchange is not confined
to the surface layers of the solid and that slow diffusion into the
bulk solid occurs, creating a space charge distribution in the solid
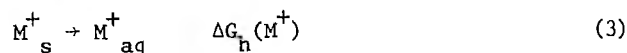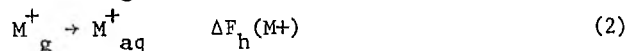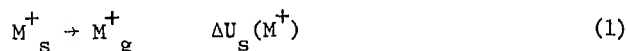phase.

Non-Reactive Ionic Solids

Non-reactive ionic solids may acquire their surface charge density
and surface potential by hydration of lattice ions. This mechanism
was first suggested and analyzed by deBruyn and Agar (14) and later by
Roman, Fuerstenau, and Seidel (15). Basically, the argument is that
for simple uni-univalent ionic solids, which must have equal surface
distribution of cation and anion on the cleavage plane, the sign of the
surface potential developed in a saturated solution can be explained
by the relative magnitudes of gaseous hydration free energies, ΔF_h, of
the ions which constitute the crystal lattice. This concept is demon-
strated for the silver halides as shown in Table 1. The free energies
of hydration of gaseous ions are from Hunt (16).

Table 1. Sign of the Surface Charge for
Silver Halides Predicted by Consideration
of the Hydration Free Energy of Gaseous Ions.

Salt	K_{sp}	PZC pAg	$-\Delta F_h^-$ (kcal/mole)	$-\Delta F_h^+$ (kcal/mole)	Sign of Surface Potential Predicted	Experimental
AgCl	1.6×10^{-10}	4.0	83.0	105.4	Negative	Negative
AgBr	7.7×10^{-13}	5.4	76.0	105.4	Negative	Negative
AgI	1.5×10^{-16}	5.5	66.7	105.4	Negative	Negative

Roman, Fuerstenau, and Seidel (15) extended this concept with good
success to explain the surface charge of highly soluble alkali halides.
Of course, with such attendant high ionic strengths in these systems,
direct confirmation of surface potentials was not possible; rather the
sign was inferred from particle-particle interactions and the flotation
response with both anionic and cationic collectors. The inferred signs
of the surface potential compared well with what would be predicted
solely from consideration of the hydration energies of the respective
gaseous ions which constitute the crystal lattice as shown by selected
examples presented in Table 2.

In spite of the good success of this correlation, clearly the ana-
lysis is limited and does not give a realistic representation of the
physical system. If hydration of lattice ions is the only mechanism
of charge generation operative, the physical process of charge genera-
tion may be represented more accurately by considering the relative
energies of the following reactions for a uni-univalent ionic solid,
MX:

$$M^+_s \rightarrow M^+_g \qquad \Delta U_s(M^+) \tag{1}$$

$$M^+_g \rightarrow M^+_{aq} \qquad \Delta F_h(M+) \tag{2}$$

$$\overline{M^+_s \rightarrow M^+_{aq} \qquad \Delta G_h(M^+)} \tag{3}$$

$\Delta U_s(M^+)$ and $\Delta F_h(M+)$ are the surface binding energy and the gaseous hydration free energy of the cation, M^+. $\Delta G_h(M^+)$ is the hydration free energy of the surface ion,

$$\Delta G_h(M^+) = \Delta U_s(M^+) + \Delta F_h(M^+) \tag{4}$$

Similarly, for the anion X^-,

$$\Delta G_h(X^-) = \Delta U_s(X^-) + \Delta F_h(X^-) \tag{5}$$

Depending on whether $\Delta G_h(M^+)$ or $\Delta G_h(X^-)$ is more negative, the corresponding ion will hydrate to a greater extent and the surface will acquire the charge of the other ion. It is evident that, if the surface binding energies, ΔU_s, for cation and anion are equivalent, the difference in the hydration energies of the respective surface ions is accounted for by the difference in hydration energies of the gaseous ions.

Now, for ionic solids, the surface binding energy, ΔU_s is principally electrostatic and can be calculated from the coulombic forces of the

Table 2. Sign of the Surface Charge for Selected Alkali Halides Predicted by Consideration of the Hydration Free Energies of Gaseous Ions.

Salt	$-\Delta F_h^-$ (kcal/mole)	$-\Delta F_h^+$ (kcal/mole)	Sign of Surface Charge Inferred from Flotation Experiments (15)
NaF	110.0	88.7	Positive
CsF	110.0	58.4	Positive
KCl	83.0	71.3	Positive
LiCl	83.0	112.5	Negative
NaBr	76.0	88.7	Negative
NaI	66.7	88.7	Negative

crystal lattice which act on the surface ions; provided the lattice geometry is known and a cleavage plane is identified. The expression for the lattice energy can be determined from Coulomb's law applied to the crystal;

$$\Delta U = -332.57 \frac{A}{r_o} Z_+ Z_- \text{ kcal/mole} \tag{6}$$

where A is the Madelung Constant, r_o is a characteristic dimension of the unit cell in angstrom units to which A is referred, and Z_+, Z_- are the cationic and anionic valences, respectively. For uni-univalent ionic solids, the Madelung Constant A is the same for the cation and the anion, either deep within the crystal or on the natural cleavage plane. This accounts for the good success in predicting the sign of the surface potential from hydration free energies of gaseous ions for simple uni-univalent ionic solids.

Evaluation of the Madelung Constant is not always an easy chore, especially for semi-infinite lattices. Therefore, before analysis of non-reactive ionic solids in detail, consider some of the general aspects regarding the Madelung Constant and computational techniques which have been proposed for its evaluation.

Madelung Constant. The potential energy of an ion with charge $Z_i e$ in the field of another ion with charge $Z_j e$ is given by Coulomb's law as;

$$U = Z_i Z_j e^2 / r_{ij}$$

where r_{ij} is the separation of the two ions. Consider a linear lattice of alternating positive and negative monovalent ions, infinite in extent, with nearest neighbor distance r.
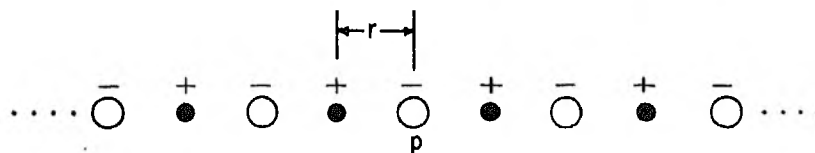
The total electrostatic potential energy of an ion at point p in the field of all the other ions is

$$U = 2\left(-\frac{e^2}{r} + \frac{e^2}{2r} - \frac{e^2}{3r} + \frac{e^2}{4r} - \cdots\right) \tag{7}$$

$$= -\frac{2e^2}{r}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \cdots\right)$$

The term in parentheses can be recognized to converge to $\log_e 2$

$$= -\frac{e^2}{r} 2\log_e 2 \tag{8}$$

The purely numerical factor $2\log_e 2$ is referred to as the Madelung Constant, after the investigator who first evaluated it (17).

At first glance it would seem that the direct summation over the individual charges could easily be carried out in two or three dimensions. As it turns out such a summation is quite sensitive to the growth geometry imposed by the summation, i.e., the summation series may or may not converge. Even if the potential sum converges it will converge to a value dependent on the shape of the mathematical crystal when the summation is stopped. This is attributed to the conditionally convergent nature of the series representing the Madelung Constant. There are many ways of circumventing this difficulty. Some methods (18, 19, 20,21,22) substitute a continuous distribution of charge for the ions and employ mathematical manipulations to achieve quick convergence. Other techniques (23,24) directly sum over neutral groups in the ionic lattice. Although most of these are ingenious methods, they are difficult to apply to surfaces (semi-infinite lattice); especially when the surface is monoionic (consisting of ions of the same charge).

THEORY AND DISCUSSION

A computational technique is described which allows the straightforward calculation of Madelung Constants for both infinite and semi-infinite lattices. The Surface Madelung Constant thus determined may be used to predict the sign of the surface potential for non-reactive ionic solids. The silver chloride and calcium fluoride systems are analyzed taking into consideration the surface binding energies. Eventually the analysis may be refined to enable the calculation of points of zero charge for non-reactive ionic solids.

Computational Technique

Similar to the approach of Evjen (23) and Frank (24), the main objective is to divide the ionic lattice into identical, neutral groups. The critical feature of the computational technique to be described is that the selection of neutral groups must be such that the potential due to each group, or array, at large distances from the reference point, diminishes faster than can be compensated for by the increasing number of such groups as the crystal "grows." Since the number of groups increases with the cube of a linear dimension of the lattice, it is evident that the potential due to each group must fall off with the fourth or higher power of its distance from the point at which the potential is being evaluated in order to assure that the lattice potential sum will converge.

To illustrate the potential-distance dependency, consider the charge array of two members shown on the top of the next page:
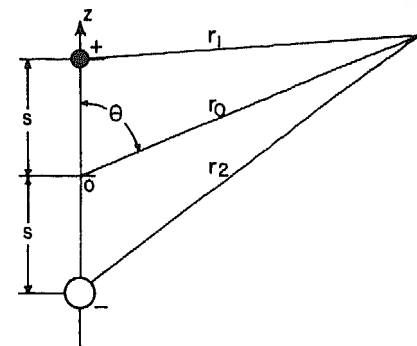
If ε_1 is the potential at p due to the positive charge at $z = s$, then using the cosine law;

$$\varepsilon_1 = \frac{e}{r_1} = \frac{e}{(r_o^2 + s^2 - 2r_o s\cos\theta)^{1/2}} \qquad (9)$$

If $r_o \gg s$, the radical may be expanded in Taylor's series;

$$\varepsilon_1 = \frac{e}{r_o}[1 + \frac{s}{r_o}\cos\theta + (\frac{s}{r_o})^2 \frac{3\cos^2\theta - 1}{2} + (\frac{s}{r_o})^3 \frac{5\cos^3\theta - 3\cos\theta}{2} + \ldots] \qquad (10)$$

Similarly, the potential ε_2 at p due to the negative charge at $z = -s$ is;

$$\varepsilon_2 = -\frac{e}{r_o}[1 - \frac{s}{r_o}\cos\theta + (\frac{s}{r_o})^2 \frac{3\cos^2\theta - 1}{2} - (\frac{s}{r_o})^3 \frac{5\cos^3\theta - 3\cos\theta}{2} + \ldots] \qquad (11)$$

Hence the potential at p due to this pair of charges (a dipole) is just

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$
$$= \frac{2es}{r_o^2}\cos\theta + \frac{es^3}{r_o^4}(5\cos^3\theta - 3\cos\theta) + \qquad (13)$$

terms of even powers of r_o.

For $r_o \gg s$, only the first term is significant and is called the dipole potential, and the pair of charges is said to possess a dipole moment.

It is seen that the potential sum over dipoles would not necessarily converge because of the slower decay of potential (r_o^{-2}) than is required.

If the array consists of two opposing dipoles on the z axis, the
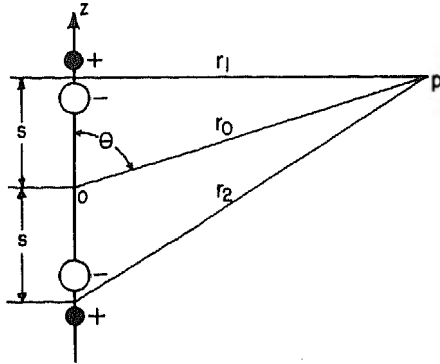
potential at p is

$$\varepsilon = \frac{es^2}{r_o^3} (3\cos^2\theta - 1) + \text{higher order terms} \qquad (14)$$

The dipole term vanishes and the array is then said to possess only a quadrupole moment (a tensor), provided $r_o >> s$. Again, the potential sum over quadrupoles would not necessarily converge because the potential decay is with r_o^{-3}.

By choosing appropriate numbers of, and charges for the lattice positions of an array, the monopole, dipole, and quadrupole potential contribution can be eliminated and the lattice sum of potential will decay with r_o^{-4} and become absolutely convergent. The calculations are much simpler when the charge arrays are linear and symmetric. For obvious reasons, these arrays shall be referred to as repeating units, which must be overlapped to reproduce the lattice at macroscopically interior points.

Infinite Lattice. Now consider the ionic crystals sodium chloride (fcc), cesium chloride (bcc), and calcium fluoride (fcc with respect to calcium and simple cubic with respect to fluoride). The crystal structures and interatomic spacings are presented in Figure 1, together with selected repeating units and their direction. The potential sum over these units is absolutely convergent as dictated by previous arguments and for a given repeating unit the limit of the sum is independent of the geometry of growth imposed by the summation procedure.

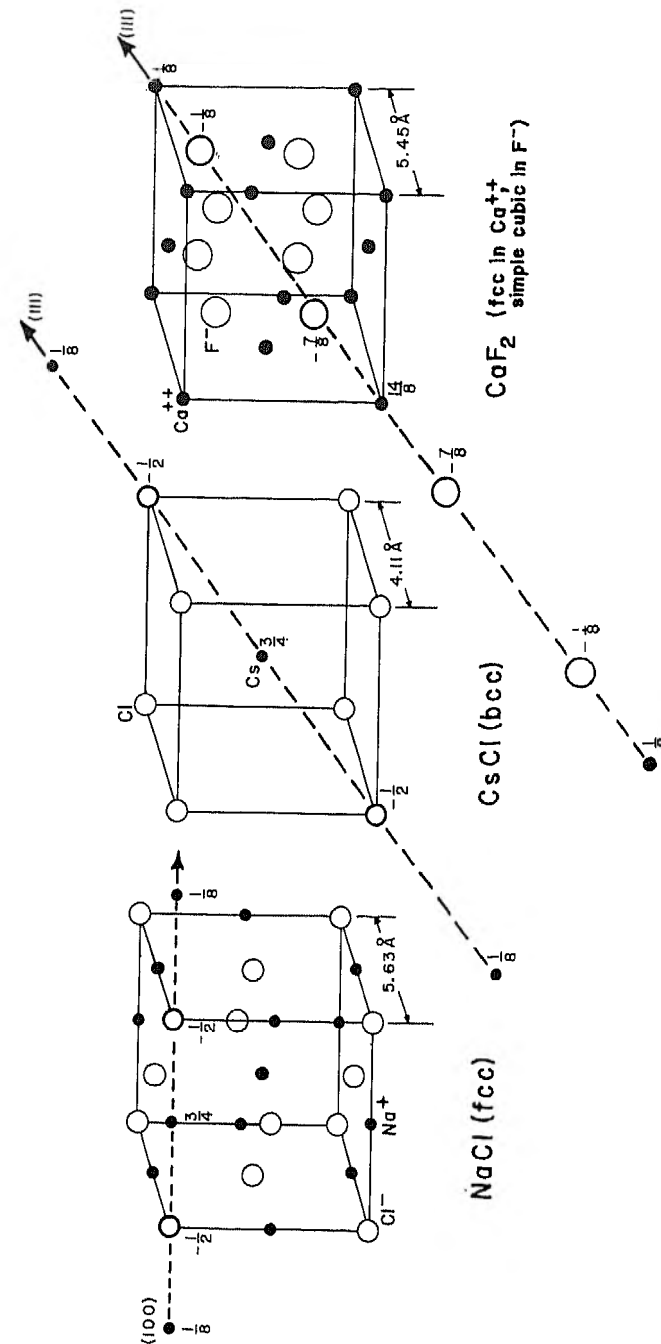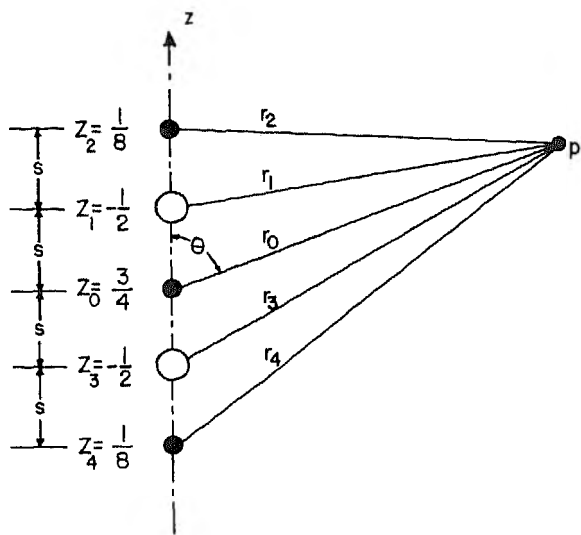The following calculation for the NaCl repeating unit, illustrates

Figure 1. Crystal structures for NaCl, CsCl, and CaF2 illustrating the selected linear repeating units, their orientation, and the charge distribution in their repeating unit array.

how the monopole, dipole, and quadrupole potential contributions are eliminated and that the lattice sum of potential will converge for the selected repeating unit.

Expressing all distances (except the interionic spacing s) in terms of r_o, and using the cosine law and Taylor's expansion as before, the potential at point p due to each charge is evaluated;

$$\epsilon_o = \frac{z_o e}{r_o} \tag{15}$$

$$\epsilon_1 = \frac{z_1 e}{r_o} [1 + (\frac{s}{r_o})\cos\theta + (\frac{s}{r_o})^2 \frac{3\cos\theta-1}{2} + (\frac{s}{r_o})^3 \frac{5\cos^3\theta-3\cos\theta}{2}$$

$$+ (\frac{s}{r_o})^4 \frac{35\cos^4\theta-30\cos^2\theta+3}{8} \ldots] \tag{16}$$

$$\epsilon_2 = \frac{z_1 e}{r_o} [1 + (\frac{2s}{r_o})\cos\theta + (\frac{2s}{r_o})^2 \frac{3\cos\theta-1}{2} + (\frac{2s}{r_o})^3 \frac{5\cos^3\theta-3\cos\theta}{2}$$

$$+ (\frac{2s}{r_o})^4 \frac{35\cos^4\theta-30\cos^2\theta+3}{8} + \ldots] \tag{17}$$

$$\epsilon_3 = \frac{z_3 e}{r_o} [1 - (\frac{s}{r_o})\cos\theta + (\frac{s}{r_o})^2 \frac{3\cos^2\theta-1}{2} - (\frac{s}{r_o})^3 \frac{5\cos^3\theta-3\cos\theta}{2}$$

$$+ (\frac{s}{r_o})^4 \frac{35\cos^4\theta-30\cos^2\theta+3}{8} \ldots] \tag{18}$$

$$\epsilon_4 = \frac{z_4 e}{r_o} [1 - (\frac{2s}{r_o})\cos\theta + (\frac{2s}{r_o})^2 \frac{3\cos^2\theta-1}{2} - (\frac{2s}{r_o})^3 \frac{5\cos^3\theta\cos\theta}{2}$$

$$+ (\frac{2s}{r_o})^4 \frac{35\cos^4\theta-30\cos^2\theta+3}{8} + \ldots] \tag{19}$$

The total potential at p is, with $z_1 = z_3$, $z_2 = z_4$;

$$\epsilon = \epsilon_0 + \epsilon_1 + \epsilon_2 + \epsilon_3 + \epsilon_4 \tag{20}$$

$$= \frac{e}{r_o} (z_0 + z_1 + z_2 + z_3 + z_4) + \frac{e}{r_o} [(2z_1+8z_2)(\frac{s}{r_o})^2$$

$$(\frac{3\cos^2\theta-1}{2})] + \frac{e}{r_o} [(2z_1+32z_2)(\frac{s}{r_o})^4 (\frac{35\cos^4\theta-30\cos^2\theta+3}{8})]+\ldots \tag{21}$$

Substituting the numerical values for the charges, the first two terms vanish and for $r_o >> s$,

$$\epsilon = \frac{3es^4}{r_o^5} (\frac{35\cos^4\theta-30\cos^2\theta+3}{8}) \tag{22}$$

The potential is seen to be proportional to r_o^{-5} which means that the potential sum of the selected repeating unit will be absolutely convergent. However, as noted by Harris (25), although the limit of the potential sum is unique for a given repeating unit, it is not necessarily the correct Madelung sum.

Any finite sample assembled from repeating units has a surface possessing a dipole moment per unit area, although the repeat units themselves have no such moment (no internal dipole contribution to the lattice sum). The magnitude and sign of the surface dipole moment is characteristic of the repeating unit. Now, the potential, ϵ, due to the dipolar surface, approaches a limit as the sample grows indefinitely because the r^{-2} potential decay from a unit surface dipole area is just compensated by the r^2 dependence of the surface

area. For a sufficiently large sample such that the summation has sufficiently converged, the difference between the direct sum V^+ (around the cation, say) and the surface contribution ξ must then be the potential due to an infinite lattice, infinite in the sense of having no surface. This difference, A, is presumed to be the Madelung Constant. Figure 2 and Equation (23) illustrate the point.

$$V^+ = A + \xi \qquad (23)$$

Using sodium chloride as an example, V^+ is the direct sum around the sodium site, A is the Madelung Constant, ξ is the surface contribution. For the sodium chloride lattice, the Madelung Constant is the same whether evaluated around a Na^+ or Cl^- site, whereas the surface contribution, ξ, must be equal, but opposite in sign for the two reference sites. Hence, if V^- is the direct sum around the Cl^- site, then

$$V^- = A - \xi \qquad (24)$$

Adding Equations (23) and (24),

$$A = \frac{1}{2}(V^+ + V^-) \qquad (25)$$

Noting that calcium is divalent and fluoride is monovalent, similar arguments for calcium fluoride give

$$A = \frac{1}{2}(V^+ + 2V^-) \qquad (26)$$

In general, for a binary ionic lattice $X_m Y_n$

$$A = \frac{1}{2}(mV^+ + nV^-) \qquad (27)$$

potential due to a large assembly of repeating units = potential due to an infinite lattice + potential due to a dipolar surface
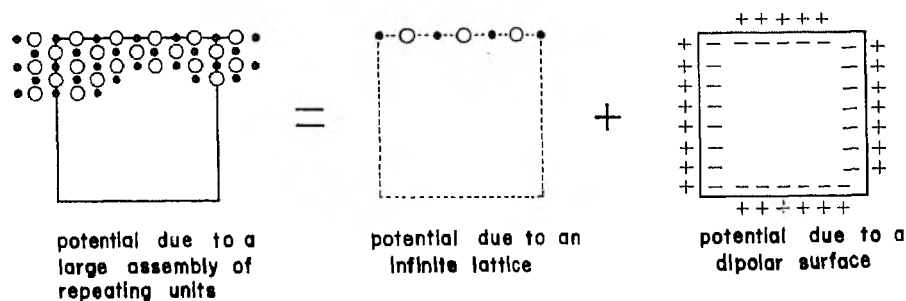
Figure 2. The converged potential sum for a lattice array of charges consists of a potential contribution due to an infinite lattice and a potential contribution due to a dipolar surface.

provided m and n have no common factor. Thus, the Madelung Constant is just half the total of potential sums around each constituent of an ionic "molecule."

To test this contention, the repeating units presented in Figure 1 were arranged with respect to selected reference ions in concentric cubical shells for NaCl and CsCl and rhombohedral shells for CaF_2. The choice of growth shape is immaterial. A computer was used to obtain the direct sums, V^+ and V^-, and the Madelung Constants were evaluated according to Equation (27). After nine shells, the computed constant for NaCl was 1.747560, which compares well with the accepted value of 1.747564. For CaF_2, the computed constant was 2.909143, accurate to six figures. Sometimes the convergence was quite rapid. Four shell summation for CsCl gave 1.7625, accurate to four figures.

Semi-Infinite Lattice. Most importantly this computational technique can be extended to include the determination of the Surface Madelung Constant for semi-infinite lattices. Consider the simple case of NaCl. After obtaining the direct sums V^+ and V^-, the dipolar surface contribution ξ is calculated from Equations (23) and (24):

$$\xi = \frac{1}{2}(V^+ - V^-) \qquad (28)$$

Now, let a <100> plane pass through the sodium reference ion. Proceeding as before, a sum of potentials, V_s^+, around this surface sodium ion which excludes the contributions from all points lying on one side of the plane can be determined. When sufficient convergence is attained, this procedure will exclude exactly half of the dipolar surface contribution, ξ. Subtracting $\frac{1}{2}\xi$ from V_s^+ yields the Madelung Constant A_s for a <100> surface sodium ion on a semi-infinite lattice:

$$A_s = V_s^+ - \frac{1}{2}\xi \qquad (29)$$

Note that $\frac{1}{2}\xi$ does not include dipole contribution, if any, from the <100> surface itself. Such a contribution is part of the Surface Madelung Constant. For NaCl, Equation (29) gives A_s = 1.66, close to the value of 1.67 calculated by Levine and Mark (26) with a method which is applicable only to electroneutral planes such as the NaCl <100>.

For non-electroneutral surface planes, the method of calculation of Levine and Mark (26) fails. However, our computational technique involving judicious selection of repeating units should accurately describe all types of surface planes. Consider the <111> plane of CaF_2 which consists entirely of fluoride ions as shown by the sectioned perspective in Figure 3. Equation (29) easily computes the Surface Madelung Constants for this surface and gives 1.26 for the surface fluoride ions and 3.01 for the subsurface calcium ions. No published values are known for the purpose of comparison.

Non-Reactive Ionic Solids

On the basis of the foregoing computational technique for the determination of Surface Madelung Constants, the surface binding energy, ΔU_s, for both anion and cation can be evaluated from Equation (6)

$$\Delta U_s = - 332.57 \frac{A_s}{r_o} Z_+ Z_- \text{ kcal/mole} \qquad (6)$$

using the appropriate Surface Madelung Constant. The overall energies for the hydration of surface ions can then be determined according to Eqs. (4), (5), using appropriate values for the hydration energies ΔF_h of gaseous ions as given in the literature (16);

$$\Delta G_h = \Delta F_h + \Delta U_s \qquad (30)$$

Sign of Surface Potential. Silver chloride in its saturated solution exhibits a negative surface potential. As mentioned previously, this has been explained by the more negative hydration free energy of gaseous silver ions than that of gaseous chloride ions. This correlation works fairly well and values for a series of silver halides are presented in Table 1. If we extend this argument to fluorite, CaF_2, the hydration free energy of gaseous Ca^{++} (-362 kcal/mole) is more nega-
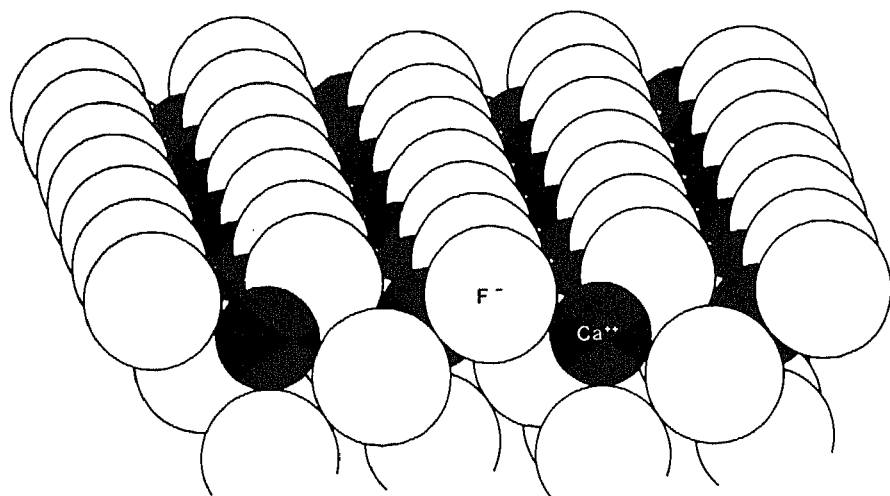

Figure 3. Perspective of the <111> cleavage surface of fluorite. Topmost layer is fluoride ions, followed next by a (subsurface) calcium layer.

tive than that of F^- (-110 kcal/mole) [all gaseous hydration free energies are from ref. 16], which would suggest that in the absence of specific chemical interactions fluorite should exhibit a negatively charged surface. However, it has been shown by Miller and Hiskey (27) that fluorite exhibits a rather large positive surface potential (ζ = +60 mv) in the absence of specific chemical interactions (e.g. surface carbonation).

Consequently, as discussed previously, this simple correlation of the sign of surface potential with hydration free energies of gaseous ions is not adequate to explain even on a qualitative basis the experimental results for a more complex non-reactive ionic solid. Using the computational technique developed, the Surface Madelung Constants for the <111> plane of fluorite are 3.01 for Ca^{++} and 1.26 for F^- both referred to the 1.36 angstrom unit distance, which represents one fourth of the unit cube dimension. From Equation (6) these represent surface binding energies of 1462 kcal/mole for Ca^{++} and 615 kcal/mole for F^-. From Equation (30):

$$\Delta G_h (Ca^{++}) = \Delta F_h(Ca^{++}) + \Delta U_s(Ca^{++})$$

$$= -362 + 1462 = 1100 \text{ kcal/mole} \qquad (31)$$

$$\Delta G_h(F^-) = \Delta F_h(F^-) + \Delta U_s(F^-)$$

$$= -110 + 615 = 505 \text{ kcal/mole} \qquad (32)$$

the free energy of hydration of the surface fluoride is more negative (less positive) than the free energy of hydration of surface calcium. The fluoride ion should preferentially hydrate and leave a positively charged CaF_2 surface, which is what has been observed experimentally (27). On a qualitative basis it appears that this analysis may be well suited for understanding the mechanism whereby non-reactive ionic solids develop a surface potential, provided that hydration of lattice ions is the only charge generation mechanism operative.

Point of Zero Charge. Consideration of surface energy terms should not only allow the prediction of the sign of the surface potentials for complex, non-reactive ionic solids in their saturated solution, but conceivably should allow for the estimation of the PZC by the use of the following fundamental relationships illustrated for a uni-univalent ionic solid, MX, at its PZC.

$$[M^+]_{aq}[X^-]_{aq} = K_{sp}, \text{ solubility product} \qquad (33)$$

$$[M^+]_{aq}/[M^+]_s = K_+, \text{ equilibrium constant for Equation 2} \qquad (34)$$

$$[X^-]_{aq}/[X]_s = K_-, \text{ equilbrium constant for Equation 3} \qquad (35)$$

$$[X^-]_s = [M^+]_s \quad \text{PZC condition} \tag{36}$$

From these expressions it can be shown for a uni-univalent ionic solid that the PZC should be, in terms of the cation concentration:

$$[M^+]_{aq} = [\frac{K_{sp} K_+}{K_-}]^{1/2} \tag{37}$$

For a case study of a uni-univalent ionic solid, consider AgCl. The Ag^+ and Cl^- have identical Madelung Constants on the <111> surface, 1.67 referred to 2.81 Angstrom unit cell side. Thus we have, in conjunction with hydration free energy data for gaseous ions (16):

$$\Delta G_h(Ag^+) = \Delta F_h(Ag^+) + \Delta U_s(Ag^+)$$

$$= -105.4 + 198.5$$

$$= 93.1 \text{ kcal/mole} \tag{38}$$

$$\Delta G_h(Cl^-) = -82.9 + 198.5 \tag{39}$$

$$= 115.6 \text{ kcal/mole}$$

From the relationships:

$$K_+ = e^{-\Delta G_h(Ag^+)/RT} = 7.98 \times 10^{-69} \tag{40}$$

$$K_- = e^{-\Delta G_h(Cl^-)/RT} = 3.02 \times 10^{-85} \tag{41}$$

and $K_{sp} = 1.56 \times 10^{-10}$ (42)

The PZC can be calculated from Equation 37:

$$[Ag^+]_{aq} = (\frac{1.56 \times 10^{-10} \times 7.98 \times 10^{-69}}{3.02 \times 10^{-85}})^{1/2} = 2030\underline{M} \tag{43}$$

which is obviously high by many orders of magnitude in that the reported PZC for AgCl is $(Ag^+)_{aq} = 10^{-4}\underline{M}$. The PZC calculation is quite sensitive to the gaseous hydration free energies because of the exponential relationship. If the gaseous hydration free energy of silver ion reported by Roman, et. al. (15), $\Delta F_h(Ag^+) = -87$ kcal/mole, is used to determine K_+ in Equation 40, then:

$$K_+ = 1.57 \times 10^{-64} \tag{44}$$

and

$$[Ag^+]_{aq} = 3.98 \times 10^{-4}\underline{M} \tag{45}$$

which is much closer to the observed PZC.

For CaF_2, a MX_2 non-reactive solid, a parallel calculation for the PZC in terms of the fluoride ion concentration gives an extremely high fluoride ion concentration that exceeds physical limits. However, the unreasonable PZC value does support the experimental observations that the surface potential of CaF_2 is not sensitive to the fluoride ion concentration even at concentrations of 0.1$\underline{M}$.

These calculations indicate that the quantitative analysis of the surface charge generated by non-reactive ionic solids needs further refinement. One possible effect which has been neglected in the analysis is the effect of lattice substitution and defect structure which appears to be important in the AgCl system (28) but seems to have no significance in the CaF_2 system (29). The analysis presented in this paper is based on a relatively simple, hard sphere model of the lattice. Further refinement of the surface binding energy, ΔU_s, is possible by taking into consideration van der Waals dispersion forces, repulsion forces, surface relaxation, and ionic deformations.

The more rigorous expression for the interaction of charged spheres is the extended Born-Mayer equation;

$$U_{ij} = Z_i Z_j e^2 R_{ij}^{-1} - a R_{ij}^{-6} - b R_{ij}^{-8} + c \exp[-R_{ij}/p] \tag{46}$$

of which only the first term has been considered. The next two terms are the van der Waals dispersion terms. The last term is the repulsive term with adjustable parameters c and p. All terms, except the first, converge rapidly and it is necessary to sum only over the nearest neighbors through the fifth.

Further refinement of the calculation by considering these effects may allow for the quantitative analysis of non-reactive ionic solids. Implicit in the PZC calculation is the fact that the ionic surface state is referred to a vacuum, which is not an accurate representation. In essence, this means that the Surface Madelung Constant calculation probably should be modified to take into consideration the surface hydration force field. Qualitatively, a partially hydrated surface ion can result in an increase in the surface binding energy which corresponds to a decrease in the PZC. Research on the magnitude of this effect is in progress.

SUMMARY AND CONCLUSIONS

The necessity of considering the binding energy of surface ions in the analysis of surface charge generation by complex, non-reactive ionic solids has been demonstrated. The determination of surface binding energies was made possible by the calculation of Surface

Madelung Constants with a new, relatively straightforward computational technique involving direct summation of critically selected neutral charge arrays. The criterion for the structure of the neutral charge array is that the charge array has no quadrupole or lower moment potential contribution to the lattice sum of potential. This condition is sufficient to assure absolute convergence of the lattice sum of potential and the direct determination of Surface Madelung Constants. Further refinement of the analysis appears to be required in order to quantitatively determine the point of zero charge for non-reactive ionic solids.

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