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NOTES

BINARY CATION-EXCHANGE REACTIONS

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Different conventions are used to write binary exchange reactions between cations of unlike charges (Sposito 1984). There is often a "seemingly arbitrary" use of cation equivalent fractions rather than cation mole fractions in the selectivity constant expressions (McBride 1994). The intent of this Note is use configurational entropy calculations in the cation-exchange process to obtain an apparent equilibrium constant that 1) is consistent with configurational entropy calculations, 2) eliminates the confusion on using end-member mole fractions versus cation equivalent fractions, 3) predicts the observed change in the conventional selectivity constant favoring more site occupancy of the higher valence cation as its site occupancy increases (McBride 1994) and 4) is consistent with the 2-parameter Langmuir power-exchange function used to fit experimental data (Langmuir 1997).

BINARY CATION EXCHANGE

In the literature, binary exchange reactions involving divalent and monovalent cations are usually written between end-member solid-solution components with unequal numbers of exchange sites (McBride 1994, Equation [3.21]):

$$M^{2+} + 2BSed = 2B^{+} + MSed_2 \qquad [1]$$

The end members BSed and $MSed_2$ form the solid solution and they contain 1 and 2 negative exchange sites, respectively. The selectivity constant for Equation [1] is usually defined following the Gaines-Thomas convention, which uses cation-equivalent fractions (X) on the exchange sites (Gaines and Thomas 1953) (McBride 1994, Equation [3.23]):

$$K_{GT} = [(a_{B^+})^2/a_{M^{2+}}][X_M/(X_B)^2] \qquad [2]$$

where a is an aqueous activity and K_{GT} is the Gaines-Thomas selectivity constant. In practice, the aqueous activity is often approximated by the molality or molarity in Equation [2] (Stumm and Morgan 1981, Equation 45).

An alternative selectivity constant for Equation [1] follows the Vanselow convention, which uses cation mole fractions ($\mathbf{X}$) on the exchange sites to define a selectivity constant K_v (Vanselow 1932). Equation [3] uses the mole fractions of $MSed_2$ and BSed, which are identical to the mole fractions of M^{2+} and B^+ on the exchange sites:

$$K_v = [(a_{B^+})^2/a_{M^{2+}}][\mathbf{X}_{MSed_2}/(\mathbf{X}_{BSed})^2] \qquad [3]$$

The thermodynamic equilibrium expression of Equation [1] can be written in terms of activities, a, for the aqueous components and the ideal activities, a^o, and activity coefficients, λ, for the end-member solid solution components:

$$K_a = [(a_{B^+})^2/a_{M^{2+}}][a^o_{MSed_2}/(a^o_{BSed})^2][\lambda_{MSed_2}/(\lambda_{BSed})^2] \qquad [4]$$

in which K_a, the thermodynamic equilibrium constant of Equation [1], is dependent upon the standard states of the components. The activity a of a solid component is related to a^o by:

$$a = a^o\lambda \qquad [5]$$

where λ accounts for deviations from ideal mixing such as steric effects on the placement of cations. The term a^o is usually assumed to equal the mole fraction in the solid solution. As reiterated below, a^o is computed from ΔS_{conf}, the increase in configurational entropy due to ideal mixing on the lattice sites.

The question arise as to which selectivity constant, Equation [2] or [3], is consistent with the thermodynamic equilibrium expression, Equation [4]. The activity ratio of the solid components in Equation [4] can be combined with the thermodynamic equilibrium constant to make an apparent equilibrium constant, $K_a[(\lambda_{BSed})^2/\lambda_{MSed_2}]$. If this apparent equilibrium constant is equal to K_{GT}, then:

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$$[a^{\circ}_{MSed_2}/(a^{\circ}_{BSed})^2] = [X_M/(X_B)^2] \quad [6]$$

And if the apparent equilibrium constant is equal to K_v, then:

$$[a^{\circ}_{MSed_2}/(a^{\circ}_{BSed})^2] = [\mathbf{X}_{MSed_2}/(\mathbf{X}_{BSed})^2] \quad [7]$$

ΔS_{conf} is calculated for different mixing scenarios to determine $a^{\circ}_{MSed_2}/(a^{\circ}_{BSed})^2$ to validate Equations [6] and [7].

By definition of an ideal mixture for a 2-component lattice:

$$\Delta S_{conf} = -R(\mathbf{X}_1 \ln a^{\circ}_1 + \mathbf{X}_2 \ln a^{\circ}_2) \quad [8]$$

where R is the gas constant and $\mathbf{X}$ is a mole fraction (equal to the moles of the component divided by the total moles in the mixture). Boltzmann's relation, applied to random mixing on the lattice sites, is:

$$\Delta S_{conf} = (R/A_v)\ln[\Omega_{mix}/(\Omega_1\Omega_2)] \quad [9]$$

A_v is Avogadro's number, Ω_{mix} is the number of distinguishable permutations in the mixture and Ω_1 and Ω_2 are the number of distinguishable permutations in the pure end members. The permutations are based on the assumptions defining ideal mixing and are computed using the multinomial coefficient and Stirling's approximation. Following the procedure of Temkin (1945), Equation [9] is recast in the form of Equation [8], and the ideal activity terms are obtained by comparison (Stoessell 1979, 1984). The computation of configurational entropy of mixing is covered in standard thermodynamic textbooks (Denbigh 1981), and only the results are given below. In this study, *the same assumptions used in the mixture to define mixing on the lattice sites were also used in the pure end members.*

The solid solution is formed by mixing N end-member components of $MSed_2$ and BSed in which $N_{MSed_2} + N_{BSed} = A_v$. The exchange sites can be filled with or without maintaining local electrostatic balance. The absence of local electrostatic balance implies random mixing of $N_{M^{2+}}$ cations and N_{B^+} cations with N_E empty sites on the lattice. Equation [9] can be shown to be:

$$\Delta S_{conf} = -R[\mathbf{X}_{MSed_2}\ln(X_M)^2 + \mathbf{X}_{BSed}\ln(X_B)] \quad [10]$$

leading to:

$$a^{\circ}_{MSed_2}/(a^{\circ}_{BSed})^2 = [X_M/X_B]^2 \quad [11]$$

The maintenance of local electrostatic balance requires random mixing of M^{2+} as part of a unit of 2 sites in which 1 site is empty. Equation [9] can be shown to become:

$$\Delta S_{conf} = -R[\mathbf{X}_{MSed_2}\ln(\mathbf{X}_{MSed_2}) + \mathbf{X}_{BSed}\ln(\mathbf{X}_{BSed})] \quad [12]$$

leading to:

$$a^{\circ}_{MSed_2}/(a^{\circ}_{BSed})^2 = \mathbf{X}_{MSed_2}/(\mathbf{X}_{BSed})^2 \quad [13]$$

Neither Equation [11] nor [13] is equal to Equation [6]; however, Equation [13] is equal to Equation [7]. Hence, for cation exchange between monovalent and divalent cations involving solid-solution end members with unequal numbers of exchange sites, the assumption of local electrostatic balance leads to the use of cation mole fractions on the exchange sites (Vanselow convention) in Equation [3]. No mixing scenario leads to the use of cation equivalent fractions (Gaines-Thomas convention) in Equation [2].

An alternative to Equation [1] is to use end members in the solid solution with equal numbers of exchange sites. The resulting reaction for cation exchange of B^+ with M^{2+} follows the Gapon convention (Gapon 1933) with integer subscripts:

$$M^{2+} + B_2Sed_2 = 2B^+ + MSed_2 \quad [14]$$

Each of the end-member components (B_2Sed_2 and $MSed_2$) forming the solid solution contain 2 lattice sites.

The thermodynamic equilibrium expression of Equation [14], written in terms of a for the aqueous components and a° and λ for the end-member components in the solid solution, is:

$$K_b = [(a_{B^+})^2/a_{M^{2+}}][a^{\circ}_{MSed_2}/a^{\circ}_{B_2Sed_2}][\lambda_{MSed_2}/\lambda_{B_2Sed_2}] \quad [15]$$

in which K_b is a thermodynamic equilibrium constant dependent upon the standard states of the components.

The solid solution is formed from mixing N end-member components of $MSed_2$ and B_2Sed_2 in which $N_{MSed_2} + N_{B_2Sed_2} = A_v$. Cations could be mixed on the lattice sites with or without maintaining local electrostatic balance. The presence of local electrostatic balance implies exchange of units of 2 adjacent sites, containing 1 M^{2+} cation and an empty site with 2 B^+ cations. Under these conditions, Equation [9] can be shown to become:

$$\Delta S_{conf} = -R[\mathbf{X}_{MSed_2}\ln(\mathbf{X}_{MSed_2}) + \mathbf{X}_{B_2Sed_2}\ln(\mathbf{X}_{B_2Sed_2})] \quad [16]$$

leading to:

$$a^{\circ}_{MSed_2}/a^{\circ}_{B_2Sed_2} = [\mathbf{X}_{MSed_2}/\mathbf{X}_{B_2Sed_2}] = [X_M/X_B] \quad [17]$$

where the cation-equivalent fractions were substituted for the end-member mole fractions because they are identical.

Substituting Equation [17] into Equation [15] gives:

$$K_b = [(a_{B^+})^2/a_{M^{2+}}][X_M/X_B](\lambda_{MSed_2}/\lambda_{B_2Sed_2}) \quad [18]$$

The expression for K_b in Equation [18] assumes standard states for the end-members having local electrostatic balance.

An apparent equilibrium constant, K_{app}, can be defined from Equation [18], equal to $K_b[\lambda_{B_2Sed_2}/\lambda_{MSed_2}]$, making:

$$K_{app} = [(a_{B^+})^2/a_{M^{2+}}][X_M/X_B] \quad [19]$$

K_{app}, like K_{GT} and K_v in Equations [2] and [3], predicts the observed increase in site occupancy by the higher

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valance cation upon dilution of the aqueous phase (the concentration-charge effect).

K_{app} can be rewritten in terms of K_{GT} in Equation [2] as:

$$K_{app} = K_{GT}(X_B) \quad [20]$$

Assuming the ratio of activity coefficients of the solid components does not vary significantly, K_{GT} has to increase if X_M increases, to offset the decrease in X_B. This is consistent with the observed increase in K_{GT} (McBride 1994) as X_M increases.

Cations could have been mixed on the lattice sites without maintaining local electrostatic balance. The scenario is covered in the next section as a special case of the Langmuir power exchange function. The equation corresponding to Equation [17] is Equation [23] below. However, the apparent equilibrium constant defined from the process predicts a decrease, not the observed increase (mentioned above) in K_{GT} as X_M increases. Consequently, the cation-exchange process for Equation [14] appears to favor maintaining local electrostatic balance.

LANGMUIR POWER EXCHANGE FUNCTION

Langmuir (1997) reports a compilation of 25 °C and 1 atm data on binary cation exchange, including monovalent and divalent cations, in terms of an empirical power-exchange function (Langmuir 1981). In terms of Equation [14], the function is:

$$K_{ex} = (a_{B^+})^2/a_{M^{2+}}[X_M/X_B]^n \quad [21]$$

in which n varies from 0.8 to 2 and K_{ex} and n are constant over a particular aqueous composition range. Note that Langmuir's data compilation is for the reverse of Equation [14], making his tabulated exchange constants the reciprocal of that in Equation [21].

K_{ex} in Equation [21] reduces to K_{app} in Equation [19] if n is 1. A nonunit value of n could have been included in K_v in Equation [18], and consequently in K_{app} in Equation [19], by using different mixing assumptions over the 2 moles of exchange sites in a solid solution formed from A_v units of $MSed_2$ and B_2Sed_2. The value of 1 arises from the assumption of local electrostatic balance.

Without local electrostatic balance, $N_{M^{2+}}$ cations and N_{B^+} cations are randomly mixed with N_E empty sites on 2 moles of exchange sites. Equation [9] can be shown to become:

$$\Delta S_{conf} = -R[\mathbf{X}_{MSed_2}\ln(X_M)^2 + \mathbf{X}_{B_2Sed_2}\ln(X_B)^2] \quad [22]$$

leading to:

$$a^o_{MSed_2}/a^o_{B_2Sed_2} = (X_M/X_B)^2 \quad [23]$$

in which n is 2.

Partial maintenance of local electrostatic balance constrains the mixing process between these 2 extremes, producing values of n between 1 and 2. Consider the case where half the sites are mixed assuming local electrostatic balance and half the sites are mixed with random cation placement. For computational purposes, the average composition over each set of sites has to be assumed to be the same. Because an individual M^{2+} cation and an empty site can be mixed randomly or as a unit, the assumption has to be made that they mix the same way in both the mixture and in the $MSed_2$ end member. Equation [9] can be shown to become:

$$\Delta S_{conf} = -R[\mathbf{X}_{MSed_2}\ln(X_M)^{1.5} + \mathbf{X}_{B_2Sed_2}\ln(X_B)^{1.5}] \quad [24]$$

leading to:

$$a^o_{MSed_2}/a^o_{B_2Sed_2} = (X_M/X_B)^{1.5} \quad [25]$$

in which n is 1.5.

Values of n below 1 arise from assuming that not all sites are available for exchange. Consider the removal of one tenth of the sites from mixing but maintaining local electrostatic balance over all sites. Again, for computational purposes, the average cation composition on each set of sites has to be assumed the same. Equation [9] can be shown to become:

$$\Delta S_{conf} = -R[\mathbf{X}_{MSed_2}\ln(X_M)^{0.9} + \mathbf{X}_{B_2Sed_2}\ln(X_B)^{0.9}] \quad [26]$$

leading to:

$$a^o_{MSed_2}/a^o_{B_2Sed_2} = (X_M/X_B)^{0.9} \quad [27]$$

in which n is 0.9.

For the sake of consistency, the same assumption needs to be used for all binary exchange reactions, that is, *mixing over all lattice sites, using units of equal charge on groups of adjacent sites of equivalent charge.* Deviations from this assumption are accounted for in the activity coefficients in Equation [18] and the difference from unity in the exponent in Equation [21].

SUMMARY

Binary exchange reactions between divalent and monovalent cations can be written to end-member components having unequal numbers of exchange sites (Equation [1]). The conventional selectivity constants are based on such a reaction. Increases in configurational entropy of mixing due to cations mixing on the exchange sites are consistent with the use of cation mole fractions (Equation [3]), not cation equivalent fractions (Equation [2]), in the selectivity constant.

Binary exchange reactions between divalent and monovalent cations can also be written to end-member components having equal numbers of exchange sites (Equation [14]). The end-member mole fractions are equal to the cation equivalent fractions. The assumption of local electrostatic balance produces an apparent equilibrium constant (Equation [19]) that predicts observed changes in the Gaines-Thomas selectivity constant (Equation [2]) favoring site occupancy by a higher valence cation as its site occupancy increases. The

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apparent equilibrium constant is also identical to the exchange constant in the Langmuir power-exchange function having an exponent of 1. Nonunity exponents in the Langmuir power-exchange function are explained by deviations from maintenance of local electrostatic balance and by removal of sites from mixing.

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REFERENCES

Denbigh KG. 1981. The principles of chemical equilibrium, 4th ed. New York: Cambridge Univ Pr. 494 p.

Gaines GL Jr, Thomas HC. 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. J Chem Phys 21:714–718.

Gapon EN. 1933. On the theory of exchange adsorption in soils. USSR J Gen Chem 3:144.

Langmuir D. 1981. The power exchange function: A general model for metal adsorption on geologic materials. In: Tewari TH, editor. Adsorption from aqueous solutions. New York: Plenum Pr. p 1–17.

Langmuir D. 1997. Aqueous environmental geochemistry, Upper Saddle River, New Jersey. New York: Prentice Hall. 600 p.

McBride MB. 1994. Environmental chemistry of soils. New York: Oxford Univ Pr. 406 p.

Sposito G. 1984. The thermodynamics of soil solutions. New York: Oxford Univ Pr. 223 p.

Stoessell RK. 1979. A regular solution site-mixing model for illites. Geochem Cosmochim Acta 43:1151–1159.

Stoessell RK. 1984. A regular solution site-mixing model for chlorites. Clays Clay Miner 32:205–212.

Stumm W, Morgan JJ. 1981. Aquatic chemistry, 2nd ed. New York: J. Wiley. 718 p.

Temkin M. 1945. Mixtures of fused salts as ionic solutions. Acta Physicochim USSR 20:411–420.

Vanselow AP. 1932. Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. Soil Sci 33:95–113.

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