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A TABULATION AND EVALUATION OF ION EXCHANGE DATA ON SMECTITES, CERTAIN ZEOLITES AND BASALT

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INTRODUCTION

Expandable clays (smectites) and zeolites have been suggested as engineered barrier materials for nuclear waste repositories because of their generally low permeabilities and high cation exchange capacities. In this topical report, we have tabulated and reviewed ion exchange data for clays, zeolites and basalt. Our discussion is concentrated on the expandable clays (smectites).

LITERATURE SEARCH

The literature search used the following sources:

Chemical Abstracts (1975 - 1980)
Clays and Clay Minerals (1975 - 1980)
Faraday Transactions I (1975 - 1980)
Journal of Soil Science (1975 - 1980)
Soil Science of America Proceedings (1975 - 1980)
Soil Science (1975 - 1980)
Annual Reports to the Waste Isolation Safety
  Assessment Program (1978 - 1979)
ARH-2731 (rev.) (Brownell et al., 1973)

References and bibliographies contained in each of the collected ion exchange publications were examined for additional sources of information. Ninety-two references to ion exchange data on clays (Appendix I), 22 references to ion exchange data on selected zeolites (Appendix II) and six references to ion exchange data on basalts (Appendix III) were obtained in this manner.

DATA ON ION EXCHANGE

Ion exchange data were generally available in three forms: distribution coefficients, corrected selectivity coefficients, and equilibrium constants. To illustrate the nature of these parameters, consider the following exchange equation:

$$Z_A B^{Z_B^+} + Z_A Z_B (A)_{1/Z_A} S = Z_B A^{Z_A^+} + Z_A Z_B (B)_{1/Z_B} S \qquad (1)$$

where Z_A and Z_B are the valences of cations A and B, and S refers to the solid substrate (exchanger).

Using the Gapon convention (Gapon, 1933) the thermodynamic equilibrium constant corresponding to eqn. (1) is

$$K^E_{AB} = \frac{\left[A^{Z_A^+}\right]^{Z_B}}{\left[B^{Z_B^+}\right]^{Z_A}} \cdot \frac{\left(\lambda_B \bar{N}_B\right)^{Z_A Z_B}}{\left(\lambda_A \bar{N}_A\right)^{Z_A Z_B}} \qquad (2)$$

where [ ] indicates the thermodynamic activity; λ_A and λ_B are activity coefficients and $\bar{N}_A$ and $\bar{N}_B$ are equivalent fractions of A and B on the substrate. The corrected selectivity quotient $\tilde{K}^E_{AB}$ is defined as:

$$\tilde{K}^E_{AB} = K^E_{AB} \left(\frac{\lambda_A}{\lambda_B}\right)^{Z_A Z_B} . \qquad (3)$$

The thermodynamic equilibrium constant can be evaluated from values of the corrected selectivity coefficient measured as a function of $\bar{N}_B$, i.e.,

$$\ln K_{BA} = Z_B - Z_A + \int_0^1 \ln \tilde{K}_{BA} \cdot d\bar{N}_B . \qquad (4)$$

The complete derivations of this and other pertinent ion exchange relations are given in Appendix IV.

The dimensionless distribution coefficient of A, K^D_A, used in transport modeling is defined as

$$K^D_A = \frac{m_{A,(c)}}{m_{A,(1)}} \qquad (5)$$

where $m_{A,(c)}$ and $m_{A,(l)}$ indicate respectively moles of A per unit volume of the solid (c) and liquid (l) phases. Experimentally obtained distribution coefficients are usually reported in dimensions of liters per kilogram. To transform experimentally obtained distribution coefficients to the dimensionless variety, values for the density of the solid phase and the porosity of the medium are needed.

While smectites appear to exchange completely, certain zeolites do not. In cases of incomplete ion exchange, the ion exchange isotherms must be normalized prior to calculation of thermodynamic parameters such as the equilibrium constant (Vansant and Uytterhoeven, 1971; Barrer et al., 1973).

Smectite Data

Equilibrium constants for ion exchange reactions on smectites at room temperature are listed in Table 1. All data are normalized to one equivalent of exchange; the notation $A \rightarrow B$ on the left hand side (L.H.S.) of the table means the exchange of A on the clay to B on the clay.

(1) Equilibrium constants describing monovalent-monovalent exchange sometimes differ by an order of magnitude for the same reaction on different smectites. For example, both sodium → cesium and sodium → rubidium equilibrium constants differ by, respectively, factors of 11 and nine between Wyoming and Camp Berteau montmorillonites.

(2) Equilibrium constants describing monovalent-monovalent exchange for the same reaction on the same smectite may differ by a factor of five but usually differ by less than a factor of two.

(3) Equilibrium constants describing sodium-divalent exchange and divalent-divalent exchange possess values on the order of unity.

The cause of the variability is discussed below.

In Table 2 we have listed Gibbs free energies and equilibrium constants for ion exchange reactions on Camp Berteau montmorillonite. Calculations were made for both sodium- and hydrogen-based clay. The open square symbol denotes the vacant site. Use was made of the "triangle rule" to generate the data of Table 2 from the data of Table 1. For example if K^E_{AB}, K^E_{CB} and K^E_{AC} denote thermodynamic equilibrium constants and ΔG_{AB}, ΔG_{CB} and ΔG_{AC} the corresponding free energies per equivalent of reaction for reaction (1) and for the respective reactions

$$z_C B^{z_B+} + z_B z_C (C)_{1/z_C} S = z_B C^{z_C+} + z_B z_C (B)_{1/z_B} S \qquad (6)$$

and

$$z_A C^{z_C+} + z_A z_C (A)_{1/z_A} S = z_C A^{z_A+} + z_A z_C (C)_{1/z_C} S \qquad (7)$$

Then per equivalent of reaction

$$\Delta G_{AC} = \Delta G_{AB} - \Delta G_{CB} \qquad (8)$$

where

$$\Delta G_{AC} = -RT \ln K^E_{AC}, \qquad (9)$$

$$\Delta G_{AB} = -RT \ln K^E_{AB}, \qquad (10)$$

and

$$\Delta G_{CB} = -RT \ln K^E_{BC}. \qquad (11)$$

From eqns. (8) - (11) we obtain

$$K^E_{AC} = K^E_{AB} \Big/ K^E_{CB}, \qquad (12)$$

thus,

$$\text{Log } K^E_{AC} = \text{Log } K^E_{AB} - \text{Log } K^E_{CB} . \tag{13}$$

We have also plotted sodium-based free energies of exchange, $\Delta G_{ex}(Na^+ \rightarrow B^{Z_B+})$, against the hydrated radius, the crystallographic radius, and the Debeye-Hückel mean distance of approach ($\mathring{a}$) of the cations (Figs. 1-3). The plots show little or no correlation between sodium-divalent free energies of exchange, and the three types of radii. Sodium-monovalent free energies of exchange, on the other hand, are positively correlated with crystallographic radius and negatively correlated with the mean distance of approach.

Equilibrium constants and Gibbs free energies for smectite ion exchange reactions at two temperatures are listed in Table 3. Changes in the value of the equilibrium constant range from four to 44 percent between these temperatures and are directly indicative of changes in the preference of the exchanging ions for the substrate.

Selectivity coefficients used in the calculation of equilibrium constants have been used by many authors to calculate activity coefficients of sorbed species as a function of substrate composition. Several workers (e.g., Inoue and Minato, 1979; Truesdell and Christ, 1968) have shown that activity coefficient data can be fitted with regular solution models.

Distribution coefficient data are not available in the open literature but are generally confined to reports sponsored by the Department of Energy's (DOE) Waste Isolation Safety Assessment Program (WISAP). For the most part the functional dependence of the distribution coefficient on concentration has not been tabulated by the various DOE contractors. Instead the data have usually been presented in graphical form which makes data extraction difficult.

Discussion of Smectite Data

The most useful exchange parameter is the equilibrium constant since both selectivity and distribution coefficients can be derived from it. Exchange constants for smectites are available for the major ionic components of groundwater and a few components of radioactive waste (Table 1). The difference among equilibrium constants describing the same exchange reaction on different smectites may be due to different laboratory procedures or they may be due to differences in the nature of the smectite itself.

The Effect of Laboratory Procedures on Values of the Equilibrium Ion Exchange Constant

Certain methods of pretreatment have been shown to alter the exchange properties of smectites by alteration of their surface properties. Several studies have shown that certain clay minerals possess two or more types of exchange sites (Low, 1955; Garrels and Christ, 1956; Blackmon, 1958; Schwertmann and Jackson, 1963). The pretreatment of clays often includes putting them in the hydrogen form prior to the sorption experiment. Several workers (Coleman and Harward, 1954; Eeckman and Laudelout, 1960; Coleman and Craig, 1961; Spain and White, 1961; and James and Parks, 1979) have shown that the relative proportions of exchange sites vary with the type and duration of treatment used to put the clay into the hydrogen form.

Smectites often contain intergrowths of iron and aluminum oxyhydroxides as well as organic materials. The use of chemical procedures to extract contaminants (Jackson, 1975) may lead to degradation of the smectite framework and thereby cause changes in its sorptive properties.

Exchange irreversibility can be caused by dehydration effects. Tabikh et al. (1960) demonstrated that after drying, rubidium, potassium, lithium and magnesium became difficult to exchange from montmorillonite. Van Bladel and Laudelout (1967) in a study of magnesium and barium exchange suggested that a high degree of flocculation also leads to exchange irreversibility. This suggestion was supported by the work of Barrer (1967) who showed that the rate of exchange between a flocculated calcium-montmorillonite and a hydrogen-based resin was much slower than the rate of exchange between a sodium-montmorillonite and a hydrogen-based resin. The half-time for the calcium-hydrogen reaction was 135 minutes; the half-time for the sodium-hydrogen reaction was 3.4 minutes.

Although certain laboratory procedures are known to alter the sorptive properties of smectites, it is difficult to assess their individual impacts on observed differences in exchange constants. Data on monovalent-monovalent reactions do, however, furnish us with certain indications of the magnitude of laboratory-induced effects. There are three values of the sodium-cesium exchange constant for Chambers montmorillonite (K_{AB} = 24, 21 and 38) and three values of the same exchange constant for Camp Berteau montmorillonite (K_{AB} = 33, 38 and 66). Thus these latter data indicate that procedural differences gave rise to differences in the exchange constant ranging from 15 - 100%.

The Effect of Smectite Composition on Values of the Equilibrium Ion Exchange Constant

Gast (1969, 1972) obtained free energies of exchange for the alkali metal ions on Chambers and Wyoming montmorillonites which had received the same laboratory treatment. The differences in exchange free energies between the two montmorillonites for the same ion couples ranged from 032 kcal/mole for the sodium-lithium couple to .805 kcal/mole for the sodium cesium couple These free energy differences correspond to differences in the equilibrium constant ranging from 20 to 390 percent. It is therefore clear that differences in the type of smectite can impose large differences on its sorptive properties. Chambers montmorillonite contains more magnesium and less silica and aluminum than Wyoming montmorillonite (see Table 1 in Gast, 1972) which indicates a greater degree of divalent ion substitution on octahedral sites in the Chambers montmorillonite. This results in a difference in the charge densities of the two clays with the Chambers montmorillonite containing one-third more charges per site per unit area. Gast has suggested that this difference in charge density may lead to differences in the exchange free energy through nearest neighbor interactions. Alternatively, the energy field resulting from an octahedral substitution may be different than the energy field resulting from a tetrahedral substitution. If the fields possess different preferences for the same ion/s, then differences in the exchange free energies for the same ion couple would result.

Zeolite Data

Few references giving data on ion exchange between zeolites and aqueous solutions exist (Appendix II). For example, only two references (Howery and Thomas, 1965; Chelishchev *et al.*, 1973) list exchange free energies for alkali metal ions on clinoptilolite. The data of Ames (1963a), if available in a tabulated form, could be used to extract free energies of exchange for sodium-strontium on clinoptilolite and erionite. Thermodynamic data for sodium-cesium and potassium-cessium exchange on Hector and Oregon clinoptilolite are available in Ames (1963b). Free energies of exchange on *synthetic* mordenite have been calculated for the cation pairs sodium-cesium, ammonium-potassium, ammonium-sodium, ammonium-lithium, ammonium-calcium, ammonium-strontium, ammonium-barium (Barrer and Klinowski, 1974) ammonium-manganese (II), ammonium-cobalt (II), ammonium-nickel, ammonium-copper (II), and ammonium-zinc (Barrer and Townsend, 1976). Data showing the temperature dependence of zeolite exchange constants do not appear to exist.

We also note that zeolites exhibit unique ion exchange behavior associated with ion-sieving (steric) effects. Clinoptilolite has a two-dimensional array of intersecting channels of two sizes. These channels are elliptical in cross section and have approximate dimensions of 0.79 x 0.35 nm and 0.44 x 0.30 nm; however, both sides of these channels are lined with pockets having free diameters of only 0.39 nm (Barrer and Townsend, 1976). Magnesium, strontium, and calcium have been found to not exchange completely with sodium in synthetic sodium mordenite (Wolf et al., 1971); and strontium may not completely exchange with sodium in sodium clinoptilolite (Ames, 1963). In ammonium-calcium and ammonium-strontium exchange experiments on mordenite, Barrer and Klinowski (1974) noted irreversible exchange of the two alkaline earths and attributed this effect to their strength of hydration.

Basalt Data

Sorption data on basalts are totally in the form of distribution coefficients. Most of the data have been obtained at room temperatures; however, Ames and McGarrah (1979) have also performed experiments at 60°, 150°, and 300°C. Experiments have been conducted using three types of aqueous solutions; synthetic groundwater, "pre-equilibrated" groundwater, and sodium chloride solutions.

Distribution coefficients for a wide variety of nuclear waste species have been determined. Unfortunately much of the data are not reproducible. A recent controlled-sample inter-laboratory program resulted in plutonium distribution coefficients whose values ranged over four orders of magnitude (Relyea and Serne, 1979).

A variety of chemical processes including changes in the surface state of the basalt resulting from its dissolution, precipitation of radionuclidebearing phases, as well as changes in the chemical speciation may all contribute to observed differences in the value of distribution coefficient. Not until we gain a greater understanding of the nature of the processes which govern the distribution of a radionuclide between basalt and an aqueous solution will we be able to quantify the distribution coefficient.

SUMMARY AND CONCLUSIONS

An extensive search of the literature has been made for ion exchange data on smectites, certain zeolites and basalt. One hundred and twenty references have been compiled (Appendices I-III). The data are primarily in the form of thermodynamic equilibrium constants, corrected selectivity coefficients, and distribution coefficients. With regard to smectites and zeolites, the equilibrium constant is by far the most useful parameter since the other parameters can be derived from it.

Room temperature alkali and alkaline earth metal cation ion exchange data for smectites are fairly extensive. A good correlation between the exchange free energies of alkali metal cations on Camp Berteau montmorillonite values with their Debeye-Hückel parameter was found. This correlation has also been noted for other montmorillonites (Gast 1969, 1972).

Significant differences in values of exchange constants for the same reaction on different smectites were noted. While this in part may be attributable to differences in experimental procedures, much of the variance is probably due to differences in charge densities and the effective field strengths of the smectites. Differences in field strength are related to the type and amount of substitution on intercrystalline octahedral and tetrahedral sites.

Only a few ion exchange experiments on smectites have been carried out over a range of temperatures. However, these data suggest that cation exchange selectivities are very strong functions of temperature.

Ion exchange data for zeolites are very limited. Experiments on the exchange properties of clinoptilolite and mordenite have been generally confined to alkali and alkaline earth cations although data for certain transition metal ions are also available for synthetic mordenite. The temperature dependences of zeolite exchange selectivities remain largely unknown.

Distribution coefficients for groundwater-basalt systems have been measured for a variety of elements at temperatures up to 150°C. Steady state concentrations are often never achieved either from the "sorption" or the "desorption" side even after equilibration periods of several months.

Classical models of ion exchange have been applied successfully to zeolite and smectite exchange reactions. The sorption behavior of a basalt is better treated with models of the interface which take surface ionization and complexation into account (James and Parks, 1979).

RECOMMENDATIONS

In order to achieve an adequate understanding of sorptive (ion exchange) processes which will occur in the engineered-barriers and far-field regions of a basalt nuclear waste repository more experimental data taken over a greater temperature range are needed.

Solid substrates used in the experiments should be representative of or identical to those phases which line fluid pathways in the far-field region and those phases which will be emplaced in the engineered barriers region.

Smectites and zeolites should be treated with classical models of ion exchange. Equilibrium exchange constants should be obtained for ions common to basaltic groundwaters. Complete isotherms need probably not be obtained for other elements whose concentrations can be shown to never exceed "trace" amounts. "Effective" equilibrium constants should be fitted to the data obtained in the trace regions. Data should be obtained over the temperature range 0-300°C.

Substrates whose sorptive properties arise from electrochemical reactions at the solid-liquid interface should be treated with surface ionization and complexation models (James and Park, 1979).

Pretreatment of smectites and zeolites should exclude: hydrogen-loading, rapid drying at temperatures above 100°C, and extraction procedures that induce structural alteration.

The compositions of experimental aqueous solutions should be pre-adjusted to minimize changes in solution and solid phase composition due to dissolution-precipitation processes. In certain cases the effects of these processes can be minimized by reducing the time interval between sorption measurements.

Long term studies of ion exchange kinetics should be done using a few selected chemical species. Solid substrates should include clinoptilolite and nontronite from the Pasco Basin as well as other materials considered prime candidates for engineered barriers.

Since nuclear waste contains such a large number of elements an effort must be made to group those with similar ion exchange properties. Experiments can then be performed on typical members of each group.

Computer models of radionuclide migration should at a minimum contain distribution-of-species algorithms. These algorithms will enable the calculation of concentration-dependent distribution coefficients. Consideration of the effects of competition among different species for sorptive sites should be included.

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TABLES

Table 1. Log K's of Ion Exchange Reactions on Smectites at 25±5°C. Data are for One Equivalent of Exchange.

REACTIONS	LOG K	SMECTITE	SOURCE
Monovalent → Monovalent			
Na → Cs	.792	Wyoming	Gast *et al.* (1969)
	1.38	Chambers	Gast (1972)
	1.49	Chambers	Eliason (1966)
	1.52	Camp Berteau	Cremers and Thomas (1968
	1.52	Wyoming	Shainberg and Kemper (1967)
	1.57	Camp Berteau	Robeyns *et al.* (1971)
	1.58	Chambers	Lewis and Thomas (1963)
	1.67	Bayard	Eliason (1966)
	1.72	Otay	Maes and Cremers (1978)
	1.82	Camp Berteau	Martin and Laudelout (1963)
Na → Rb	.465	Wyoming	Gast *et al.* (1969)
	.988	Chambers	Gast (1972)
	1.25	Camp Berteau	Robeyns *et al.* (1971)
	1.42	Camp Berteau	Martin and Laudelout (1963)
Na → K	.225	Wyoming	Gast *et al.* (1969)
	.246	Wyoming	Tabikh *et al.* (1960)
	.348	Belle Fourche	Tabikh *et al.* (1960)
	.398	Wyoming	Shainberg and Kemper (1967)
	.490	Utah	Tabikh *et al.* (1960)
	.531	Chambers	Gast (1972)
	.609	Camp Berteau	Martin and Laudelout (1963)
Na → Li	- .204	Wyoming	Shainberg and Kemper (1967)
	- .101	Camp Berteau	Martin and Laudelout (1963)
	- .057	Chambers	Gast (1972
	- .033	Wyoming	Gast *et al.* (1969)
	.045	Camp Berteau	Robeyns *et al.* (1971)
	.045	Wyoming	Tabikh *et al.* (1960)
Na → NH_4	.577	Camp Berteau	Martin and Laudelout (1963)
	.748	Camp Berteau	Robeyns *et al.* (1971)
	.777	Camp Berteau	Vansant and Uytterhoeven (1972)
Na → H	- .204	Otay	Foscolos and Barshad (1969)
	- .104	Colony	Foscolos and Barshad (1969)
	.176	Camp Berteau	Gilbert and Laudelout (1965)
H → NH_4	.491	Camp Berteau	Gilbert and Laudelout (1965)
H → K	.426	Colony	Foscolos and Barshad (1969)
	.690	Otay	Foscolos and Barshad (1969)

Table 1. Log K's of Ion Exchange Reactions on Smectites at 25±5°C. Data are for One Equivalent of Exchange. (Cont'd)

REACTIONS	LOG K	SMECTITE	SOURCE
Monovalent → Divalent			
Na → Fe(II)	- .385	Mississippi	Singhal *et al.* (1975)
Na → Ba	.040	Camp Berteau	Laudelout *et al.* (1968)
	.364	Chambers	Lewis and Thomas (1963)
Na → Co(II)	.143	Camp Berteau	Maes *et al.* (1975)
Na → Ni(II)	.121	Camp Berteau	Maes *et al.* (1975)
Na → Cu(II)	.121	Camp Berteau	Maes *et al.* (1975)
Na → Zn	.125	Camp Berteau	Maes *et al.* (1975)
Na → Cd	.088	Camp Berteau	Maes *et al.* (1975)
Na → Ca	.196	Otay	Maes and Cremers (1977)
Na → Sr	.121	Bayard	Eliason (1966)
Cs → Ba	-1.35	Chambers	Lewis and Thomas (1963)
Cs → Sr	-1.28	Chambers	Gaines and Thomas (1955)
	-1.47	Bayard	Eliason (1966)
K → Ca	.038	Japanese	Inoue and Minato (1979)
NH_4 → Mg	- .751	Camp Berteau	Laudelout *et al.* (1968)
NH_4 → Ca	- .730	Camp Berteau	Laudelout *et al.* (1968)
NH_4 → Sr	- .724	Camp Berteau	Laudelout *et al.* (1968)
NH_4 → Ba	- .686	Camp Berteau	Laudelout *et al.* (1968)
Divalent → Divalent			
Ca → Cu(II)	- .009	Wyoming	El-Sayed *et al.* (1970)
Ca → Sr	.019	Mississippi	Kown and Ewing (1969)
Ca → Mg	- .087	Wyoming	Levy and Shainberg (1972)
Ca → Ni(II)	- .054	India	Singhal *et al.* (1976)
Mg → Sr	.059	Mississippi	Kown and Ewing (1969)
Mg → Zn	- .064	Mississippi	Singhal and Kumar (1977)
Mg → Ni(II)	- .108	India	Singhal *et al.* (1976)

Table 2. Standard Gibbs Free Energies and Equilibrium Constants for Ion Exchange Reactions on Camp Berteau Montmorillonite (ΔG^o in Kcal/eq.).

REACTION	ΔG^o	Log K	REACTION	ΔG^o	Log K
*H→□	6.2	-4.5	H→□	6.2	-4.5
Na→H	-.240	.176	H→H	0.00	0.00
**Na→Li	.137	-.101	H→Li	.378	-.277
Na→Na	0.00	0.00	H→Na	.240	-.176
Na→K	-.831	.609	H→K	-.591	.433
**Na→Rb	-1.70	1.25	H→Rb	-1.46	1.07
**Na→Cs	-2.14	1.57	H→Cs	-1.90	1.39
Na→Mg	.0353	.0259	H→Mg	.275	-.202
Na→Ca	.00633	.00464	H→Ca	.246	-.181
Na→Sr	-.000937	.000687	H→Sr	.240	-.176
Na→Ba	-.054	.040	H→Ba	.184	-.135
Na→Co	-.190	.139	H→Co	.0449	-.0329
Na→Ni	-.165	.121	H→Ni	.0757	-.0555
Na→Cu	-.165	.121	H→Cu	.0757	-.0555
Na→Zn	-.170	.125	H→Zn	.0712	-.0522
Na→Cd	-.120	.0880	H→Cd	.122	-.0897
**Na→NH_4	-1.06	.777	H→NH_4	-.820	.601

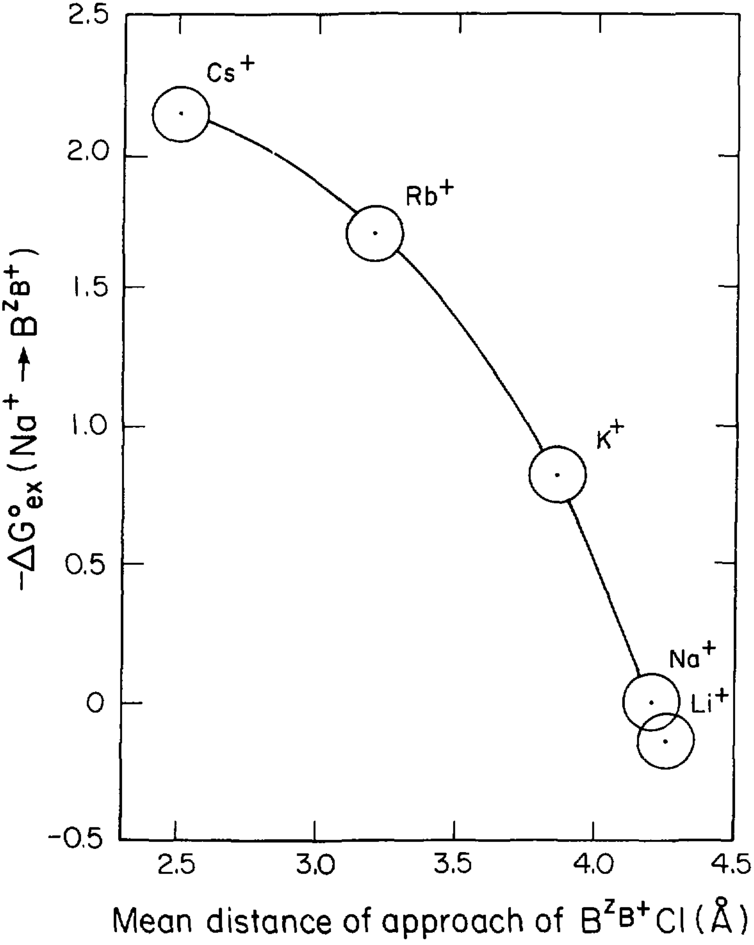
*Weighted average of data for two-sited Belle Fourche montmorillonite (see Silva *et al*, 1979)

**Data from Robeyns *et al* (1971).

Table 3. Changes in the Free Energy of Ion Exchange for Smectites as a Function of Temperature

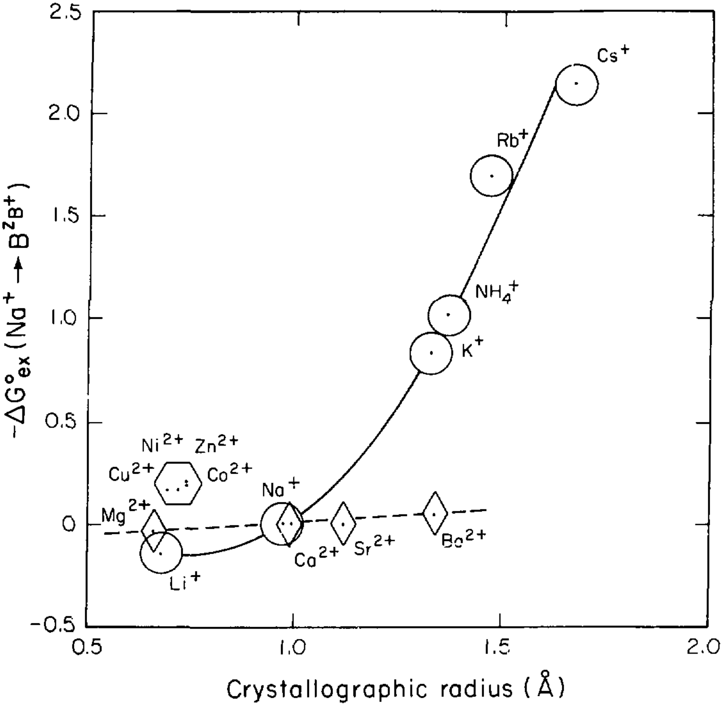
REACTION	ΔG_1	(T_1)	K_1	ΔG_2	(T_2)	K_2	SUBSTRATE	SOURCE
Mg → Zn	.0874	(30°C)	.862	.0666	(60°C)	.894	Mississippi	Singhal and Kumar (1977)
Ca → Cu(II)	.0125	(30°C)	.979	.192	(50°C)	.723	Wyoming	El-Sayed _et_ _al_. (1970)
Ca → Ni	.0737	(30°C)	.883	.150	(60°C)	.776	India	Singhal _et_ _al_. (1976)
Mg → Ni	.148	(30°C)	.779	.181	(60°C)	.737	India	Singhal _et_ _al_. (1976)
Na → Fe(II)	.525	(30°C)	.412	.547	(60°C)	.397	Mississippi	Singhal _et_ _al_. (1975)
K → Ca	.0525	(35°C)	.915	.393	(90°C)	.515	Japan	Inoue and Minato (1979)
Na → NH_4	.732	(25°C)	.291	.867	(55°C)	.231	Camp Berteau	Vansant and Uytterhoeven (1972)

FIGURES



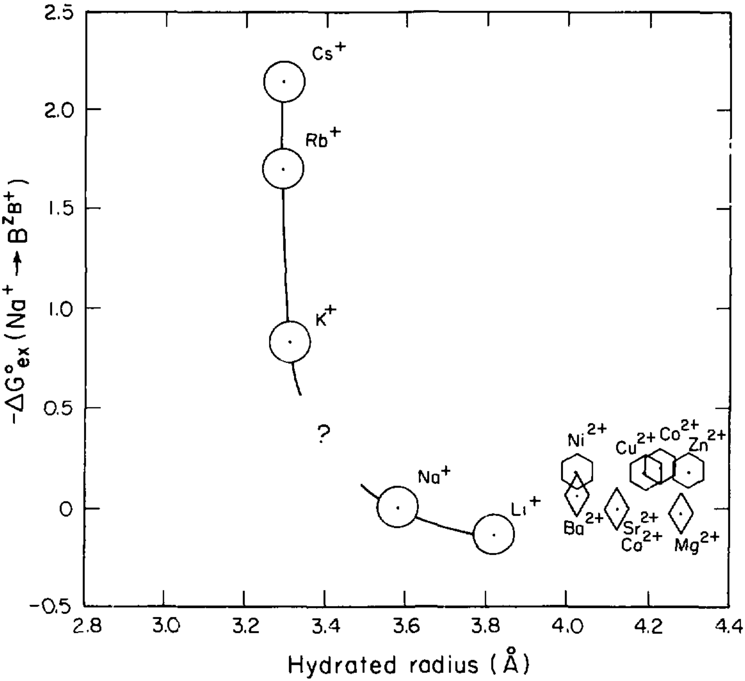
XBL 805-7078

Figure 1



XBL 805-7076

Figure 2



XBL 805-7077

Figure 3

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APPENDIX IV Thermodynamic Theory of Ion Exchange Equilibria for Systems Having Fixed Cation Exchange Capacities

The thermodynamic theory of ion exchange equilibria between smectites or zeolites and aqueous solution was originally developed by various authors including Högfeldt (1952) and Gaines and Thomas (1953). The treatment of the effect of water activity on ion exchange selectivity was further expanded by Laudelout and coworkers (Laudelout and Thomas, 1965; Laudelout et al., 1971; Laudelout et al., 1972). In more recent times, the ion exchange formalism has been extended to cation exchangers possessed of multiple sites and also to cation exchangers which exhibit incomplete exchange (Barrer and Klinowski, 1978; Barrer et al., 1973).

Essentially all thermochemical calculations using ion exchange isotherm data have been made using the method of Gaines and Thomas (1953). Because of its widespread application, this method and certain of its extensions will be reviewed.

Assume we have a certain amount of exchanger, S^-, in equilibrium with an aqueous solution containing two cations A^{Z_A+} and B^{Z_B+} where Z_A and Z_B are the absolute values of the valence. The ions are assumed to exchange in equivalent amounts and the exchanger is assumed to possess a constant cation exchange capacity.

Component stoichiometries can be formulated in two ways. The components can either be written as $A_{1/Z_A}S$ or AS_{Z_A}. The concentrations of $A_{1/Z_A}S$ and AS_{ZA} can be expressed respectively by equivalent fraction N_A and mole fraction X_A. Consider an ion exchanger containing $m_A A^{Z_A+}$, $m_B B^{Z_B+}$ and $(m_A Z_A + m_B Z_B)S^-$ Depending on our choice of components we have either $m_A Z_A (A)_{1/Z_A} S$, $m_B Z_B (B)_{1/Z_B} S$ or $m_A AS_{Z_A}$, $m_B AS_{Z_A}$. The equations defining N_A, N_B and X_A, X_B are:

$$N_A = \frac{m_A Z_A}{m_A Z_A + m_B Z_B} \;;\; N_B = \frac{m_B Z_B}{m_A Z_A + m_B Z_B} \;;\; N_A + N_B = 1 \qquad (1)$$

$$X_A = \frac{m_A}{m_A + m_B} \;;\; X_B = \frac{m_B}{m_A + m_B} \;;\; X_A + X_B = 1 \qquad (2)$$

From eqns. (1) and (2) we find:

$$\frac{N_A}{N_B} = \frac{X_A Z_A}{X_B Z_B} \qquad (3)$$

Using the "equivalents" formulation for components, the exchange reaction can be written:

$$z_A B^{z_B+} + z_A z_B (A)_{1/z_A} S = z_B A^{z_A+} + z_A z_B (B)_{1/z_B} S. \qquad (4)$$

The mass action expression corresponding to eqn. (4) is

$$K^E_{AB} = \frac{\left[A^{Z_A+}\right]^{Z_B} \left[B_{1/Z_B} S\right]^{Z_A Z_B}}{\left[B^{Z_B+}\right]^{Z_A} \left[A_{1/Z_A} S\right]^{Z_A Z_B}} \qquad (5)$$

where [ ] signifies activity. The relationship between concentrations and activities of components is defined as:

$$\left[A_{1/Z_A} S\right] = \lambda_A \bar{N}_A \;;\; \left[A_{1/Z_B} S\right] = \lambda_B \bar{N}_B \qquad (6)$$

where λ_A and λ_B are activity coefficients in the equivalents convention. The thermodynamic constant K^E_{AB} can therefore be expressed as

$$K^{E}_{AB} = \frac{\left[A^{Z_A+}\right]^{Z_B}}{\left[B^{Z_B+}\right]^{Z_A}} \cdot \frac{\left(\lambda_B \bar{N}_B\right)^{Z_A Z_B}}{\left(\lambda_A \bar{N}_A\right)^{Z_A Z_B}} \qquad (7)$$

The equilibrium quotient (corrected selectivity coefficient in the Gapon convention; Gapon, 1933) corresponding to eqn. (7) is

$$\tilde{K}^{E}_{AB} = K^{E}_{AB} \left(\frac{\lambda_A}{\lambda_B}\right)^{Z_A Z_B} \qquad (8)$$

Using the "moles" formulation for components, the exchange reaction can be written

$$Z_A B^{Z_B+} + Z_B AS_{Z_A} = Z_B A^{Z_A+} + Z_A BS_{Z_B} \qquad (9)$$

The mass action expression corrresponding to eqn. (9) is

$$K^{M}_{AB} = \frac{\left[A^{Z_A+}\right]^{Z_B} \left[BS_{Z_B}\right]^{Z_A}}{\left[B^{Z_B+}\right]^{Z_A} \left[AS_{Z_A}\right]^{Z_B}} \qquad (10)$$

The relationship between concentrations and activities of components is defined as

$$\left[AS_{Z_A}\right] = \eta_A \bar{X}_A \;;\; \left[BS_{Z_B}\right] = \eta_B \bar{X}_B \qquad (11)$$

where η_A and η_B are activity coefficients in the moles convention. The thermodynamic constant K^{M}_{AB} can therefore be expressed as

$$K_{AB}^{M} = \frac{\left[A^{Z_A+}\right]^{Z_B}\left(\eta_B\bar{X}_B\right)^{Z_A}}{\left[B^{Z_B+}\right]^{Z_A}\left(\eta_A\bar{X}_A\right)^{Z_B}} \tag{12}$$

and the equilibrium quotient (corrected selectivity coefficient in the Vanselow convention; Vanselow, 1932) corresponding to eqn. (12) is

$$\bar{K}_{AB}^{M} = K_{AB}^{M}\,\frac{(\eta_A)^{Z_B}}{(\eta_B)^{Z_A}} \;. \tag{13}$$

In order to obtain the relations between the parameters derived above using the "equivalents" and the "moles" conventions we first note the following relationship between component molecular weights:

$$AS_{Z_A} = Z_A \cdot \left(A_{1/Z_A}\right)S \;;\; BS_{Z_B} = Z_B \cdot \left(B_{1/Z_B}\right)S \tag{14}$$

The chemical potentials of the components are

$$\begin{aligned}
\mu_{A,E} &= \mu_{A,E}^{\circ} + RT\ln\lambda_A\bar{N}_A\\
\mu_{B,E} &= \mu_{B,E}^{\circ} + RT\ln\lambda_B\bar{N}_B\\
\mu_{A,M} &= \mu_{A,M}^{\circ} + RT\ln\eta_A\bar{X}_A\\
\mu_{B,M} &= \mu_{B,M}^{\circ} + RT\ln\eta_B\bar{X}_B
\end{aligned} \tag{15}$$

From eqns. (14) and (15) it follows that

$$\mu_{A,M} = Z_A\mu_{A,E} \; ; \; \mu_{B,M} = Z_B\mu_{B,E} \tag{16}$$

Since the standard states are the same for both formalisms, i.e. the pure components,

$$\overset{\circ}{\mu}_{A,M} = Z_A\overset{\circ}{\mu}_{A,E} \; ; \; \overset{\circ}{\mu}_{B,M} = Z_B\overset{\circ}{\mu}_{B,E} \tag{17}$$

Using eqns. (15), (16) and (17) we find the following relations between activities:

$$\eta_A\bar{X}_A = \left(\Lambda_A\bar{N}_A\right)^{Z_A} \; ; \; \eta_B\bar{X}_B = \left(\Lambda_B\bar{N}_B\right)^{Z_B} . \tag{18}$$

From eqns. (7), (12) and (18) we obtain the following relationship between equilibrium constants:

$$K^{E}_{AB} = K^{M}_{AB} \tag{19}$$

From eqns. (3), (8), (13), (18) and (19) we find the following relationship between equilibrium coefficients (corrected selectivity coefficients):

$$\tilde{K}^{M}_{AB} = \tilde{K}^{E}_{AB}\left(\frac{Z_A}{Z_B}\right)^{Z_AZ_B} \cdot \frac{\bar{X}_A^{\{Z_B(Z_A-1)\}}}{\bar{X}_B^{\{Z_A(Z_B-1)\}}} \tag{20}$$

From eqn. (20) it is clear that $\tilde{K}^{M}_{AB} = \tilde{K}^{E}_{AB}$ if and only if $Z_A = Z_B = 1$. These relationships derived originally by Hogfeldt (1952) have recently been reiterated by Sposito (1977).

Essentially all calculations of the Gibbs standard free energies of ion exchange have been made using the method of Gaines and Thomas (1953). Their method utilizes the "equivalents" convention and was derived for a model defined solely in terms of directly measurable quantities. In their most general derivation Gaines and Thomas (1953) considered a thermodynamically closed system containing two cations, A^{Z_A+} and B^{Z_B+}, the single anion L^{Z_L+}, and the solvent denoted by the subscript (s). The solid is assumed to have a constant cation exchange capacity and is capable of adsorbing anions and solvent.

In terms of the total energy, E, the condition for equilibrium at constant total entropy is

$$\delta E_{(c)} + \delta E_{(1)} + \delta E_{(g)} = 0 \tag{21}$$

where the subscripts (c), (1) and (g) refer respectively to the solid, liquid, and vapor phases. The following additional constraints are imposed on the chemical species

$$\delta m_{A,(1)} + \delta m_{A,(c)} = 0 \tag{22}$$

$$\delta m_{B,(1)} + \delta m_{B,(c)} = 0 \tag{23}$$

$$Z_A \delta m_{A,(c)} + Z_B \delta m_{B,(c)} - Z_L \delta m_{L,(c)} = 0 \tag{24}$$

$$Z_A \delta m_{A,(1)} + Z_B \delta m_{B,(1)} - Z_L \delta m_{L,(1)} = 0 \tag{25}$$

$$\delta m_{s,(c)} + \delta m_{s,(1)} + \delta m_{s(g)} = 0 \tag{26}$$

It follows that

$$\delta m_{L,(1)} + \delta m_{L,(c)} = 0 \; . \tag{27}$$

At equilibrium the equality of pressure, temperature, and chemical potential, μ, for each of the thermodaynmic components throughout the system leads to the following expressions:

$$Z_L \mu_{A,(c)} + Z_A \mu_{L,(c)} = Z_L \mu_{A,(1)} + Z_A \mu_{L,(1)} \tag{28}$$

$$Z_L\mu_{B,(c)} + Z_B\mu_{L,(c)} = Z_L\mu_{B,(l)} + Z_B\mu_{L,(l)} \tag{29}$$

which when taken together give rise to its usual expression for the equilibrium condition, i.e.,

$$Z_B\mu_{A,(c)} + Z_A\mu_{B,(l)} = Z_A\mu_{B,(c)} + Z_B\mu_{A,(l)} \ . \tag{30}$$

We consider a mass of exchanger corresponding to one exchange equivalent, so that

$$Z_A m_{A,(c)} + Z_B m_{B,(c)} - Z_L m_{L,(c)} = 1 \ , \tag{31}$$

and define

$$\bar{N}_A = Z_A m_{A,(c)} \ ; \ \bar{N}_B = Z_B m_{B,(c)} \ ; \ \bar{N}_L = Z_L m_{L,(c)} \tag{32}$$

so that

$$\bar{N}_A + \bar{N}_B - \bar{N}_L = 1 \ . \tag{33}$$

We choose to write the expressions for the chemical potentials in the customary manner,

$$\mu_{A,(c)} = \mu^{\circ}_{A,(c)} + RT\ln\bar{N}_A\lambda_A \tag{34}$$

$$\mu_{B,(c)} = \mu^{\circ}_{B,(c)} + RT\ln\bar{N}_B\lambda_B \tag{35}$$

$$\mu_{A,(l)} = \mu^{\circ}_{A,(l)} + RT\ln m_{A,(l)}\gamma_A \tag{36}$$

$$\mu_{B,(l)} = \mu^{\circ}_{B,(l)} + RT\ln m_{B,(l)}\gamma_B \tag{37}$$

$$\mu_{L,(c)} = \mu^{\circ}_{L,(c)} + RT\ln\bar{N}_{L,(c)}f_L \ . \tag{38}$$

The mass action expression corresponding to eqn. (30) taken together with eqns. (34) - (37) is

$$K^{E}_{AB} = \frac{\left(\bar{N}_A\right)^{Z_B} \left(m_{B,(1)}\right)^{Z_A}}{\left(\bar{N}_B\right)^{Z_A} \left(m_{A,(1)}\right)^{Z_B}} \cdot \frac{\left(\Lambda_A\right)^{Z_B} \left(\gamma_B\right)^{Z_A}}{\left(\Lambda_B\right)^{Z_A} \left(\gamma_A\right)^{Z_B}} \quad . \tag{39}$$

The Gibbs-Duhem equation for the four-component system is

$$m_{A,(c)} d\ln\bar{N}_A\Lambda_A + m_{B,(c)} d\ln\bar{N}_B\Lambda_B + m_{L,(c)} d\ln\bar{N}_L\Lambda_L + m_{s,(c)} d\ln[s] = 0 \tag{40}$$

From eqns. (28), (29) and (34) - (38) we can form the differential expressions:

$$d\ln K^{Z_L}_{LA} + d\ln\Lambda^{Z_L}_{A} + d\ln\Lambda^{Z_A}_{L} = 0 \tag{41}$$

$$d\ln K^{Z_L}_{LB} + d\ln\Lambda^{Z_L}_{B} + d\ln\Lambda^{Z_B}_{L} = 0 \tag{42}$$

in which

$$\tilde{K}^{Z_L}_{LA} = \frac{\bar{N}_A^{Z_L} \; \bar{N}_L^{Z_A}}{m^{Z_L}_{A,(1)} \; m^{Z_A}_{L,(1)} \; \gamma_A^{Z_L} \; \gamma_L^{Z_A}}$$

$$\tilde{K}^{Z_L}_{LB} = \frac{\bar{N}_B^{Z_L} \; \bar{N}_L^{Z_B}}{m^{Z_L}_{B,(1)} \; m^{Z_B}_{L,(1)} \; \gamma_B^{Z_L} \; \gamma_L^{Z_B}} \tag{43}$$

Through the relation

$$\ln K_{BA} = \ln\tilde{K}_{BA} + \ln\Lambda_A^{Z_B} - \ln\Lambda_B^{Z_A} \tag{44}$$

we define the corrected selectivity coefficient $\tilde{K}_{BA}$ so that

$$d\ln\tilde{K}_{BA} + d\ln\Lambda_A^{Z_B} - d\ln\Lambda_B^{Z_A} = 0 \tag{45}$$

Eqn. (40) together with eqns. (41) - (45) enables the elimination of the coefficients Λ and makes possible integrations which allow the evaluation of these activity coefficients in terms of experimentally obtainable parameters.

Choosing to integrate across the isothermal surface at constant $\bar{N}_L$, the resulting expressions for λ_A and λ_B are

$$
\begin{aligned}
\ln \lambda_A^{Z_B}(Q) = \ln \lambda_A^{Z_B}(a) \\
& - \left\{ N(Q) - N(a) \right\} - \bar{N}_B \ln \tilde{K}_{BA}(Q) \\
& + \bar{N}_L \left\{ \ln \tilde{K}_{LA}^{Z_B}(Q) - \ln \tilde{K}_{LA}^{Z_B}(a) \right\} \\
& + \int_a^Q \ln \tilde{K}_{BA} \cdot d\bar{N}_B - Z_A Z_B \int_a^Q m_{s,(c)} d\ln[s]
\end{aligned}
\tag{46}
$$

and

$$
\begin{aligned}
\ln \lambda_B^{Z_A}(Q) = \ln \lambda_B^{Z_A}(b) \\
& - \left\{ N(Q) - N(b) \right\} + \bar{N}_A \ln \tilde{K}_{BA}(Q) \\
& + \bar{N}_L \left\{ \ln \tilde{K}_{LB}^{Z_A}(Q) - \ln \tilde{K}_{LB}^{Z_A}(b) \right\} \\
& + \int_Q^b \ln \tilde{K}_{BA} \cdot d\bar{N}_B + Z_A Z_B \int_Q^b m_{s,(c)} d\ln[s]
\end{aligned}
\tag{47}
$$

where

$$
N \equiv Z_A Z_B \left\{ \frac{\bar{N}_A}{Z_A} + \frac{\bar{N}_B}{Z_B} + \frac{\bar{N}_L}{Z_L} \right\} .
$$

The resulting expression for the equilibrium constant defined by eqn. (30) is

$$
\begin{aligned}
\ln K_{BA} = (Z_B - Z_A)(1 + \bar{N}_L) \\
& + \ln \frac{\lambda_A^{Z_B}(a)}{\lambda_B^{Z_A}(b)} - \bar{N}_L \ln \frac{\tilde{K}_{LA}^{Z_B}(a)}{\tilde{K}_{LB}^{Z_A}(b)} \\
& + \int_a^b \ln \tilde{K}_{BA} \cdot d\bar{N}_B - Z_A Z_B \int_a^b m_{s,(c)} d\ln[s]
\end{aligned}
\tag{48}
$$

If the solid substrate is incapable of adsorbing anions, eqn. (48) reduces to:

$$\ln K_{BA} = (Z_B - Z_A) + \ln \frac{\lambda_A^{Z_B}(a)}{\lambda_B^{Z_A}(b)}$$

$$+ \int_0^1 \ln \tilde{K}_{BA} \cdot d\bar{N}_B - Z_A Z_B \int_a^b m_{s,(c)} d\ln[s] \ . \qquad (49)$$

Given our choice of standard states the second term on the R.H.S. of eqn (49) is identically zero. If in addition the activity of the solvent remains nearly constant during the substrate's transition from the pure A state to the pure B state, the last term on the R.H.S. of eqn. (49) also approaches zero, such that eqn. (49) reduces to

$$\ln K_{BA} = Z_B - Z_A + \int_0^1 \ln \tilde{K}_{BA} \cdot d\bar{N}_B \qquad (50)$$

the form used by almost all investigators to calculate K_{BA} from experimental data.