

Roberto T. Pabalan and F. Paul Bertetti

Center for Nuclear Waste Regulatory Analyses

Southwest Research Institute

6220 Culebra Road

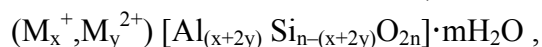
San Antonio, Texas 78238

INTRODUCTION

Zeolite minerals are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations characterized by an ability to hydrate/dehydrate reversibly and to exchange some of their constituent cations with aqueous solutions, both without a major change in structure. Because of their ion-exchange, adsorption, and molecular sieve properties, as well as their geographically widespread abundance, zeolite minerals have generated worldwide interest for use in a broad range of applications. Examples of these applications are discussed in other chapters of this book. Of particular interest in this chapter are the cation-exchange properties of zeolite minerals. Due to the favorable ion-exchange selectivity of natural zeolites for certain cations, such as Cs^+ , Sr^{2+} , and NH_4^+ , these minerals have been studied for potential use in the treatment of nuclear wastewaters (Howden and Pilot 1984; Baxter and Berghauer 1986; Robinson et al. 1995; Pansini 1996), municipal and industrial wastewaters (Kallo 1995; Pansini 1996), and acid mine drainage waters (Bremner and Schultze 1995; Zamzow and Schultze 1995). Natural zeolites have also been studied for potential use in the remediation of sites contaminated with fission products such as ^{90}Sr and $^{135,137}\text{Cs}$ (Leppert 1988; Valcke et al. 1997a; Valcke et al. 1997b) and in the remediation of soils contaminated with heavy metals (Ming and Allen, this volume). Additional interest resulted from the potential siting of a high-level nuclear waste repository at Yucca Mountain, Nevada, which is underlain by diagenetically altered, zeolite-rich (clinoptilolite, heulandite, and mordenite) rhyolitic tuffs (Broxton et al. 1986; Broxton et al. 1987) that could serve as barriers to radionuclide migration to the accessible environment.

Zeolites consist of three-dimensional frameworks of $(\text{Si},\text{Al})\text{O}_4$ tetrahedra where all oxygen ions of each tetrahedron are shared with adjacent tetrahedra. The presence of Al^{3+} in place of Si^{4+} in the structure gives rise to a deficiency of positive charge in the framework. The net negative charge is balanced by cations, principally Na^+ , K^+ , and Ca^{2+} , less frequently Li^+ , Mg^{2+} , Sr^{2+} , and Ba^{2+} , which are situated in cavities within the structure. Zeolite structures are remarkably open, and void volumes of dehydrated zeolites of almost 50% are known.

The following idealized general formula for natural zeolites has been proposed (Gottardi 1978; Gottardi and Galli 1985):



where M^+ represents monovalent cations with stoichiometry x , and M^{2+} represents divalent cations with stoichiometry y . Cations within the first set of parentheses are the exchangeable cations. Those within the brackets are the structural cations because, with oxygen, they make up the framework of the structure. The value of m gives the number of water molecules in the structure and provides an idea of the volume of the channels relative to the total volume. Normally, this number does not exceed half the number of framework oxygens, and $n/2 < m < n$ (Gottardi 1978). The $(\text{Si} + \text{Al})\text{:O}$ ratio of a zeolite is

1:2, and the number of tetrahedral Al^{3+} is equal to the sum of positive charges ($x + 2y$) of the exchangeable cations in the idealized formula. Thus, the theoretical cation-exchange capacity (CEC) is primarily a function of the charge density of the anionic structure, i.e. the degree of substitution of Al^{3+} for Si^{4+} in its tetrahedral framework. The greater the Al^{3+} substitution, the more cations are needed to maintain electrical neutrality and, hence, the higher the CEC. For example, a study by Zamzow et al. (1990) on heavy metal sorption on natural zeolites showed a linear correlation between the Si/Al ratio of the zeolite and the ion-exchange capacity for Pb^{2+} , in the order phillipsite > chabazite > erionite > clinoptilolite > mordenite. The expected CECs for several zeolite minerals based on their isomorphous substitution are listed in Table 1.

Table 1. Cation-exchange capacity (CEC) of zeolite minerals based on the number of equivalents of exchangeable cations or the number of moles of Al^{3+} in the chemical formula. Values are given in milliequivalents per gram of solid (meq/g).

<i>Zeolite</i>	<i>Typical Unit-Cell Formula*</i>	<i>CEC (meq/g)</i>
Analcime	$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$	4.5
Chabazite	$\text{Ca}_2(\text{Al}_4\text{Si}_8\text{O}_{24}) \cdot 12\text{H}_2\text{O}$	3.9
Clinoptilolite	$(\text{Na},\text{K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$	2.2
Erionite	$\text{NaK}_2\text{MgCa}_{1.5}(\text{Al}_8\text{Si}_{28}\text{O}_{72}) \cdot 28\text{H}_2\text{O}$	2.8
Faujasite	$\text{Na}_{20}\text{Ca}_{12}\text{Mg}_8(\text{Al}_{60}\text{Si}_{132}\text{O}_{384}) \cdot 235\text{H}_2\text{O}$	3.6
Ferrierite	$(\text{Na},\text{K})\text{Mg}_2\text{Ca}_{0.5}(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$	2.3
Heulandite	$(\text{Na},\text{K})\text{Ca}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$	3.2
Laumontite	$\text{Ca}_4(\text{Al}_8\text{Si}_{16}\text{O}_{48}) \cdot 16\text{H}_2\text{O}$	4.3
Mordenite	$\text{Na}_3\text{KCa}_2(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 28\text{H}_2\text{O}$	2.2
Natrolite	$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{24}\text{O}_{80}) \cdot 16\text{H}_2\text{O}$	5.3
Phillipsite	$\text{K}_2(\text{Ca}_{0.5},\text{Na})_4(\text{Al}_6\text{Si}_{10}\text{O}_{32}) \cdot 12\text{H}_2\text{O}$	4.5
Wairakite	$\text{Ca}_8(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$	4.6

*taken from Gottardi and Galli (1985)

The exchangeable cations of a zeolite are only loosely held in the anionic framework and, to a first approximation, can be removed or exchanged easily by washing the zeolite with a concentrated solution of another cation. In practice, the ion-exchange behavior of zeolites also depends on other factors, including: (1) the framework topology (channel configuration and dimensions); (2) ion size and shape (polarizability); (3) charge density of the anionic framework; (4) ionic charge; and (5) concentration of the external electrolyte solution (Barrer 1978). The diffusion character of a zeolite depends on the number of channels and their spatial configuration.¹ All other factors remaining equal, cations diffuse faster through zeolites with three-dimensional channel systems than those

¹ The kinetics of ion exchange is controlled by diffusion of ions within the crystal structure. This topic is outside the scope of this chapter, but extensive literature on the subject is available. A review of ion-exchange kinetics is given by Helfferich and Hwang (1991). Other useful references include Brooke and Rees (1968, 1969), Breck (1974), and Barrer (1980).

with one- or two-dimensional channel systems. The size of the ion, as well as the channel dimensions, determine whether or not a given cation will fit into a particular framework. For example, chabazite exhibits complete exclusion of the ions La^{3+} , $(\text{CH}_3)_4\text{N}^+$, and $(\text{C}_2\text{H}_5)_4\text{N}^+$, due to the large size of these cations (Breck 1974). Analcime, which has a dense structure and nonintersecting channels and cavities, exhibits very limited ion exchange of its Na^+ for other cations, particularly at room temperature. To some extent, high temperatures can offset the effect of large ionic radius. Thus, at elevated temperatures, Na^+ in analcime can be completely replaced by K^+ , Ag^+ , Tl^+ , NH_4^+ , and Rb^+ (Vaughn 1978).

Size considerations and the effect of the rigid nature of the zeolite framework (i.e. the nearly fixed pore volumes) can also explain the steric limitations and ion sieve properties exhibited by zeolites, such as those observed by Barrer et al. (1967). In their studies on ion exchange between Na-clinoptilolite and various alkyl-ammonium cations, Barrer et al. (1967) observed that ions small enough to enter the two main channels of clinoptilolite [e.g. NH_4^+ , CH_3NH_3^+ , $\text{C}_2\text{H}_5\text{NH}_3^+$, $(\text{CH}_3)_2\text{NH}_2^+$, and $n\text{-C}_3\text{H}_7\text{NH}_3^+$] exchange completely with Na^+ . Those small enough to enter the 10-ring channel, but too large to penetrate the 8-ring channel, are only partially exchanged [e.g. $(\text{CH}_3)_3\text{NH}^+$, $n\text{-C}_4\text{H}_9\text{NH}_3^+$, and $\text{iso-C}_3\text{H}_7\text{NH}_3^+$], whereas the largest ions [e.g. $(\text{CH}_3)_4\text{NH}_3^+$ and $\text{tert-C}_4\text{H}_9\text{NH}_3^+$] are totally excluded.

Many zeolites contain several crystallographically distinct sets of sites that can be occupied by exchangeable cations, and each site may exhibit different selectivities and ion-exchange behavior. The number of available exchange sites commonly exceeds the number of negative charges to be neutralized. Hence, the anionic charge of the framework may be neutralized when only some of the sites are occupied or when some of the sites are only partially occupied, and the occupancy factors may vary with the nature of the neutralizing cation (Barrer 1980, 1984). In addition, the entering ion does not necessarily take the position of the leaving ion (Sherry 1971; Cremers 1977). Thus, zeolites may exhibit a high degree of cationic disorder, both in terms of unoccupied sites and in terms of different distributions of cations of different kinds among the available sites.

This site heterogeneity in the zeolite is likely to manifest itself in compositional variations of the selectivities and activity coefficients of the zeolite components. As a consequence, it is difficult to predict multicomponent equilibrium exchange relations from binary data alone (Fletcher et al. 1984). Although it is theoretically possible to evaluate the contribution of the component site groups to the overall thermodynamics of exchange and to the overall equilibrium constant (Barrer 1978), Townsend (1984) questioned whether one should use measurements of ion-exchange equilibria to infer details of a particular heterogeneous site model for the exchanger, unless independent measurements that provide information on the structure and site heterogeneity are also applied to the material (e.g. X-ray diffraction, neutron diffraction, nuclear magnetic resonance, electron microscopy). Thermodynamic measurements are concerned with changes in macroscopic physical properties of the system under study, and it is difficult to infer from thermodynamic data alone the fundamental mechanisms that underlie the observed ion-exchange behavior.

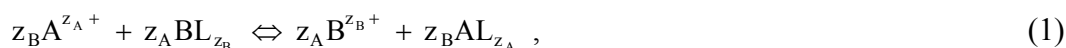
Nevertheless, thermodynamic formulations, if properly conceived, provide firm and systematic bases for understanding ion-exchange behavior and its dependence on various parameters, and these formulations serve as tools for predicting exchange equilibria under conditions not previously studied. The basic thermodynamic formulations for ion exchange are based on principles developed long ago by researchers on inorganic exchange materials, especially clays (Vanselow 1932; Gapon 1933; Kielland 1935;

Gaines and Thomas 1953). These formulations are still widely used in current ion-exchange literature, irrespective of the nature of the exchanger under study. A review of the thermodynamics of ion exchange is given in the following section.

THERMODYNAMICS OF ION EXCHANGE

Ion-exchange isotherm

For a binary ion exchange involving cations A^{z_A+} and B^{z_B+} , the basic reaction may be written as



where z_A+ and z_B+ are the valences of the respective cations, and L is defined as a portion of zeolite framework holding unit negative charge.² Anions are also present in the aqueous solution and maintain electroneutrality in that phase.³

The binary exchange equilibrium can be described conveniently by an ion-exchange isotherm, which is a plot of the equilibrium concentration of an exchanging ion in solution against the equilibrium concentration of that same ion in the zeolite at constant temperature and solution normality. The isotherm is usually plotted in terms of the equivalent cation fraction of the ion in solution against that in the solid (Dyer et al. 1981). The equivalent cationic fractions of A^{z_A+} and B^{z_B+} (\bar{E}_A and \bar{E}_B , respectively) in the zeolite phase are defined as

$$\bar{E}_A = \frac{z_A \bar{n}_A}{z_A \bar{n}_A + z_B \bar{n}_B}; \quad \bar{E}_B = \frac{z_B \bar{n}_B}{z_A \bar{n}_A + z_B \bar{n}_B} \quad (2)$$

where \bar{n}_A and \bar{n}_B are the number of moles of ions A^{z_A+} and B^{z_B+} , respectively, in the zeolite. Equivalent cationic fractions in the aqueous solution can be defined similarly as:

$$E_A = \frac{z_A n_A}{z_A n_A + z_B n_B}; \quad E_B = \frac{z_B n_B}{z_A n_A + z_B n_B} \quad (3)$$

where n_A and n_B are the number of moles of A^{z_A+} and B^{z_B+} , respectively, in the aqueous phase.

The ion-exchange isotherm can then be plotted from the equilibrium values of \bar{E}_A and E_A (or \bar{E}_B and E_B). For the binary exchange reaction shown in Equation (1),

$$E_B = 1 - E_A; \quad \bar{E}_B = 1 - \bar{E}_A \quad (4)$$

Thus, the isotherm fully defines the equilibrium at a specified temperature and solution normality.⁴

²Other studies represent the ion-exchange reaction as Equation (1b),



which can be traced to the work by Gapon (1933), is an equally valid way of expressing the binary exchange reaction (Townsend 1986). However, Equations (1) and (1b) have different reaction stoichiometries, resulting in different ion-exchange equilibrium constants and thermodynamic functions. These differences should be kept in mind when interpreting published data on ion exchange. Detailed discussions of these alternate forms are provided by Townsend (1986) and Grant and Fletcher (1993).

³In systems where the cation exhibits a strong tendency to form aqueous complexes with some anions in solution, the selectivity of the zeolite for the cation is strongly dependent on the nature of the co-anion. See, for example, Loizidou and Townsend (1987a).

⁴Equations for calculating equivalent cationic fractions and the associated uncertainties from measured solution concentrations of A^{z_A+} and B^{z_B+} and other experimental parameters are given in the appendix.

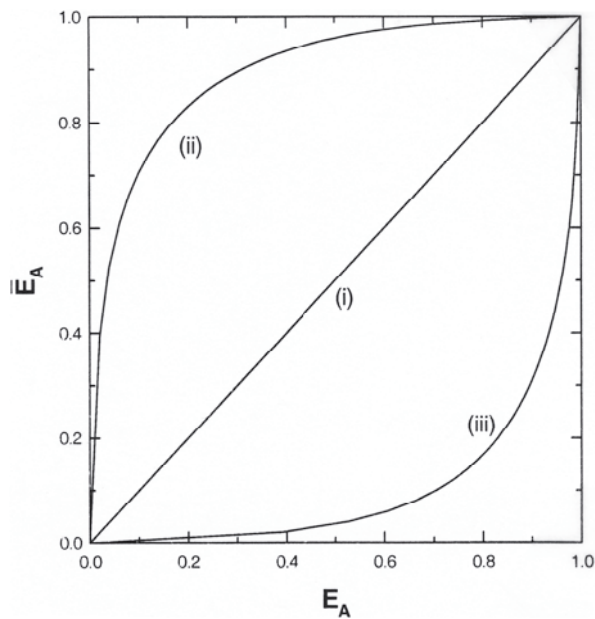


Figure 1. Examples of isotherms for the ion-exchange reaction shown in Equation (1).

Isotherm plots are convenient illustrations of the preference or selectivity of a zeolite for ion A^{z_A+} relative to ion B^{z_B+} . For example, a zeolite with equal preference for ions A^{z_A+} and B^{z_B+} will exhibit an isotherm shown by line (1) in Figure 1. Isotherm (2) illustrates the case where the zeolite prefers A^{z_A+} over B^{z_B+} , whereas isotherm (3) is for the case where B^{z_B+} is preferred over A^{z_A+} . In some cases, the zeolite exhibits a preference for A^{z_A+} over B^{z_B+} at one composition range and a reversed selectivity at another composition range. An example of selectivity reversal is shown in Figure 2 in which the zeolite prefers A^{z_A+} (Sr^{2+}) at low \bar{E}_A and B^{z_B+} (Na^+) at high \bar{E}_A .

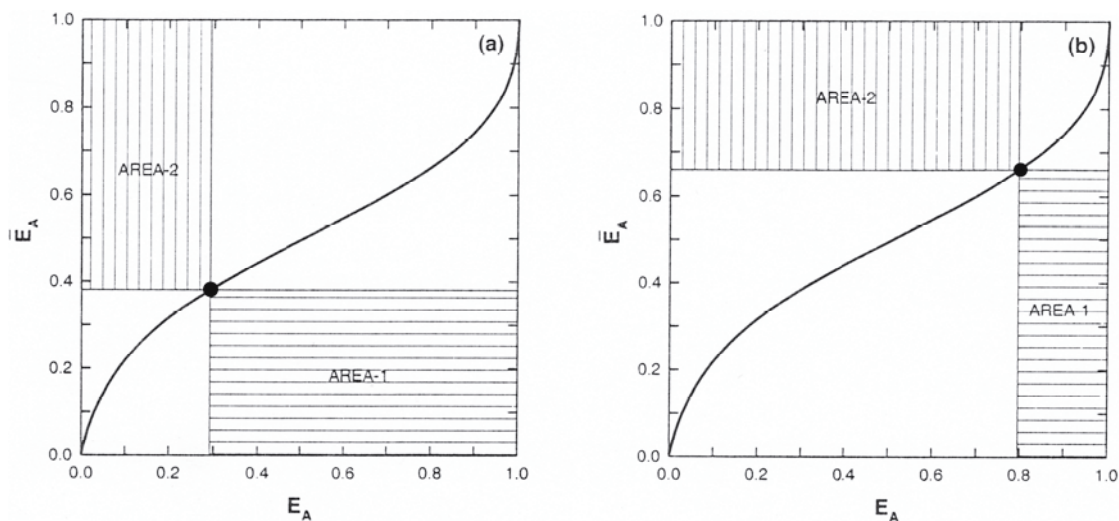


Figure 2. Ion-exchange isotherm showing selectivity reversal. The isotherm is based on data from Pabalan and Bertetti (1999) on ion exchange involving clinoptilolite and 0.5 N $\text{Sr}^{2+}/\text{Na}^+$ solutions (Cl^- anion). The zeolite prefers A^{z_A+} (Sr^{2+}) at low \bar{E}_A (Fig. 2a) and B^{z_B+} (Na^+) at high \bar{E}_A (Fig. 2b). Area-1 equals $[(1 - E_A) \cdot \bar{E}_A]$, and Area-2 equals $[E_A \cdot (1 - \bar{E}_A)]$.

Selectivity coefficient

The preference of a zeolite for ion A^{z_A+} relative to ion B^{z_B+} can be expressed in terms of a selectivity coefficient, α , which is defined as

$$\alpha = \frac{\bar{E}_A n_B}{\bar{E}_B n_A} \quad (5)$$

From Equation (3), $n_A = (z_A n_A + z_B n_B) E_A / z_A$ and $n_B = (z_A n_A + z_B n_B) E_B / z_B$. It follows that

$$\alpha = \frac{z_A}{z_B} \cdot \frac{\bar{E}_A E_B}{\bar{E}_B E_A} \quad (6)$$

or, from Figure 2,

$$\alpha = \frac{z_A}{z_B} \cdot \frac{\text{Area-1}}{\text{Area-2}} \quad (7)$$

It is apparent from Figure 2 that α can vary with the level of exchange (\bar{E}_A) (Dyer et al. 1981). The conditions for selectivity at a specified \bar{E}_A are:

- (1) when $\alpha > (z_A/z_B)$, the zeolite is selective for A^{z_A+} ;
- (2) when $\alpha = (z_A/z_B)$, the zeolite exhibits no preference; and
- (3) when $\alpha < (z_A/z_B)$, the zeolite is selective for B^{z_B+} .

The examples illustrated in Figure 2 are based on experimental data on $\text{Sr}^{2+}/\text{Na}^+$ ion exchange ($A^{z_A+} = \text{Sr}^{2+}$; $B^{z_B+} = \text{Na}^+$; $z_A/z_B = 2$). The calculated value of α is 2.97 for the data point (solid circle) shown in Figure 2a; thus, the zeolite prefers Sr^{2+} over Na^+ at this value of \bar{E}_{Sr} . The value of \bar{E}_{Sr} is higher and the calculated α is 0.99 for the data point in Figure 2b, i.e. the zeolite is selective for Na^+ relative to Sr^{2+} .

CONCENTRATION-VALENCY EFFECT

The total concentration of the aqueous solution does not have a large effect on the selectivity of the zeolite for a particular ion for exchange reactions in which the exchange ions have equal charges (e.g. Na^+ and K^+). However, when the exchange ions have different valences (e.g. Na^+ and Ca^{2+}), the ion-exchange behavior of the system depends strongly on the total concentration of the aqueous solution, and the selectivity of the zeolite for the ion of higher valence becomes progressively greater with increasing dilution. This 'concentration-valency' effect can arise universally from high dilution of the electrolyte solution independent of the exchanger phase (Barrer and Klinowski 1974a). This effect explains why Ca^{2+} can be removed from dilute aqueous solutions by synthetic ion exchangers, such as water softeners, whereas an exhausted exchanger in Ca-form can be regenerated into Na-form with concentrated NaCl solution. Figure 3 shows an example of a concentration-valency effect for ion exchange involving clinoptilolite and $\text{Sr}^{2+}/\text{Na}^+$ solutions at various solution concentrations. With increasing dilution, the isotherm becomes more rectangular and clinoptilolite exhibits increasing selectivity for Sr^{2+} relative to Na^+ .

Equilibrium constant, Gibbs free energy, and Vanselow coefficient

The thermodynamic equilibrium constant, $K_{(A,B)}$, for the ion-exchange reaction represented by Equation (1) is given by:

$$K_{(A,B)} = \frac{(\bar{a}_A)^{z_B} (a_B)^{z_A}}{(a_A)^{z_B} (\bar{a}_B)^{z_A}} \quad (8)$$

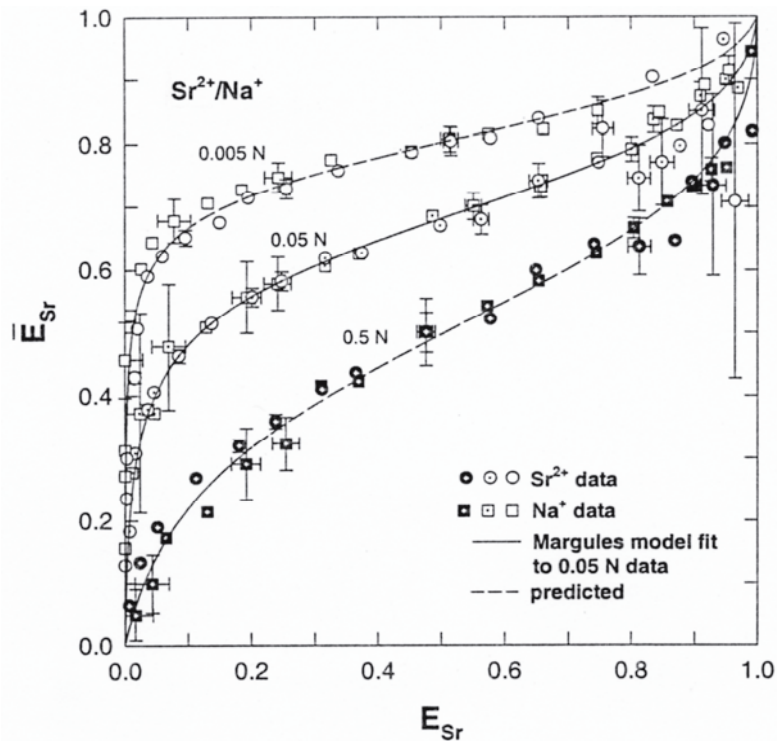


Figure 3. Isotherms for ion exchange at 298 K between clinoptilolite and $\text{Sr}^{2+}/\text{Na}^+$ solutions (0.005, 0.05, and 0.5 N; Cl^- anion). Circles and squares were calculated from Sr^{2+} and Na^+ analytical data, respectively. Some error bars, based on Sr^{2+} and Na^+ analytical uncertainties, are shown. The solid curve was fit to the 0.05 N isotherm data using a Margules solid-solution model. The dashed curves represent predicted values. Data from Pabalan and Bertetti (1999).

where a_i represents activities of the aqueous species and \bar{a}_i represents activities of the zeolite components. The standard Gibbs free energy, $\Delta G_{(A,B)}^\circ$, of ion exchange can be calculated from

$$\Delta G_{(A,B)}^\circ = -RT \ln K_{(A,B)} \quad (9a)$$

where R is the gas constant and T is temperature (Kelvin). Values of $K_{(A,B)}$ and $\Delta G_{(A,B)}^\circ$ provide an estimate of the selectivity of the zeolite for A^{z_A+} relative to B^{z_B+} . However, Colella (1996) pointed out that these thermodynamic parameters give unequivocal indications of selectivity only for ion-exchange pairs that exhibit isotherms like (2) and (3) in Figure 1. Selectivity reversals exhibited in some systems, such as shown in Figure 2, are not evident from values of $K_{(A,B)}$ and $\Delta G_{(A,B)}^\circ$ alone.

It should be noted that some studies report the standard free energy in terms of the equivalents involved in the exchange reaction, i.e.

$$\Delta G_{(A,B)}^\oplus = \frac{-RT \ln K_{(A,B)}}{z_A z_B} \quad (9b)$$

The zeolite may be considered as a solid solution of two components AL_{z_A} and BL_{z_B} (Ekedahl et al. 1950; Freeman 1961; Barrer and Klinowski 1977), where L_{z_A} is the amount of anionic framework associated with an A^{z_A+} ion and carrying anionic charge z_A^- , and L_{z_B} is the amount of framework associated with B^{z_B+} and carrying anionic charge z_B^- . The number of moles of AL_{z_A} and BL_{z_B} are then respectively equal to the

total number of moles \bar{n}_A and \bar{n}_B of ions $A^{z_A^+}$ and $B^{z_B^+}$ in the zeolite, and solid phase compositions can be described in terms of cationic mole fractions, \bar{X}_A and \bar{X}_B , defined as:

$$\bar{X}_A = \frac{\bar{n}_A}{\bar{n}_A + \bar{n}_B}; \quad \bar{X}_B = \frac{\bar{n}_B}{\bar{n}_A + \bar{n}_B} \quad (10)$$

Equation (8) may be expanded to give:

$$K_{(A,B)} = \frac{(\bar{X}_A)^{z_B} (M_B)^{z_A}}{(\bar{X}_B)^{z_A} (M_A)^{z_B}} \cdot \frac{(f_A)^{z_B}}{(f_B)^{z_A}} \cdot \frac{(\gamma_B)^{z_A}}{(\gamma_A)^{z_B}} \quad (11)$$

or,

$$K_{(A,B)} = K_{v(A,B)} \cdot \frac{(f_A)^{z_B}}{(f_B)^{z_A}} \quad (12)$$

where $K_{v(A,B)}$ is the Vanselow corrected selectivity coefficient (Vanselow 1932; Townsend 1986) defined by

$$K_{v(A,B)} = \frac{(\bar{X}_A)^{z_B} (M_B)^{z_A}}{(\bar{X}_B)^{z_A} (M_A)^{z_B}} \cdot \frac{(\gamma_B)^{z_A}}{(\gamma_A)^{z_B}} \quad (13)$$

and M_A and M_B are the molarities of $A^{z_A^+}$ and $B^{z_B^+}$ in the aqueous phase.⁵ The quantities γ_A and γ_B are single-ion activity coefficients for the aqueous cations and account for nonideal behavior in the aqueous phase. The quantities f_A and f_B are rational (i.e. in terms of mole fractions) activity coefficients for the zeolite components and account for nonideality in the zeolite phase.

Evaluation of $K_{(A,B)}$, f_A , f_B , and $\Delta G_{(A,B)}^0$

It is necessary to define the standard states of the various components to allow the evaluation of $K_{(A,B)}$, f_A , and f_B from experimental data using the Gibbs-Duhem relation. The usual standard state for the aqueous electrolyte solution external to the zeolite phase is that of a hypothetical, one molar solution referenced to infinite dilution. It has been normal practice to follow Gaines and Thomas (1953) for the exchanger phase and make the standard state for each exchanging cation the appropriate homoionic form of the zeolite in equilibrium with an infinitely dilute solution of the same cation (Sposito 1981). With that standard state, the criterion for ideal behavior in the zeolite solid solution is that $\bar{a}_i = \bar{X}_i$ for all \bar{X}_i .

The evaluation of $K_{(A,B)}$, f_A , and f_B from experimental data results from an appropriate integration of the Gibbs-Duhem relation (Argersinger et al. 1950). Together with Equation (13), the Gibbs-Duhem equation gives the following expressions for calculating the equilibrium constant and zeolite phase activity coefficients:

$$\ln K_{(A,B)} = \int_0^1 \ln K_{v(A,B)} d(\bar{E}_A) \quad (14)$$

$$\ln f_A^{z_B} = -\bar{E}_B \ln K_{v(A,B)}^* + \int_{\bar{E}_A}^1 \ln K_{v(A,B)} d(\bar{E}_A) \quad (15)$$

and

⁵Equations for calculating $\ln K_{v(A,B)}$ and the associated uncertainty from measured concentrations of $A^{z_A^+}$ and $B^{z_B^+}$ in solution are given in the appendix.

$$\ln f_B^{z_A} = \bar{E}_A \ln K_{v(A,B)}^* - \int_0^{\bar{E}_A} \ln K_{v(A,B)} d(\bar{E}_A), \quad (16)$$

where the superscript * refers to the value of $K_{v(A,B)}$ at a particular \bar{E}_i . Note that although $K_{v(A,B)}$ is defined in terms of \bar{X}_i , Equations (14) to (16) also require values of the charge fraction \bar{E}_i . The relationships between \bar{X}_i and \bar{E}_i are shown by

$$\bar{X}_A = \frac{\bar{E}_A/z_A}{\bar{E}_A/z_A + \bar{E}_B/z_B}; \quad \bar{X}_B = \frac{\bar{E}_B/z_B}{\bar{E}_A/z_A + \bar{E}_B/z_B}. \quad (17)$$

Values of $K_{(A,B)}$, $\ln f_A$, and $\ln f_B$ can be determined by graphical integration of the plot of $\ln K_{v(A,B)}$ versus \bar{E}_A , or analytically by integrating a best-fit equation to the ion-exchange data.⁶

The above thermodynamic formulations are valid for conditions where electrolyte imbibition by the solid is negligible and where changes in zeolite water activity are insignificant. The salt concentration at which imbibition for zeolites is negligible depends on the intracrystalline channel dimensions. The concentration often cited is <0.5 M, although Dyer et al. (1981) give a value of <1.0 M. The water activity terms are not significant (Barrer and Klinowski 1974a) for most cases of ion-exchange equilibria. However, for ion exchange involving concentrated electrolyte solutions, terms can be included in the equations to account for the effects of sorbed or imbibed solvent and of imbibed salts (Gaines and Thomas 1953; Townsend 1986; Grant and Fletcher 1993).

Triangle rule

If ion-exchange experiments involving cations A^{z_A+} , B^{z_B+} , and C^{z_C+} were made pairwise, self-consistency of the derived thermodynamic constants and Gibbs energies can be assessed by applying the 'triangle rule' (Howery and Thomas 1965), which can be represented by

$$[K_{(A,B)}]^{z_C} \times [K_{(B,C)}]^{z_A} \times [K_{(C,A)}]^{z_B} = 1 \quad (18)$$

and

$$z_C \Delta G_{(A,B)}^\circ + z_A \Delta G_{(B,C)}^\circ + z_B \Delta G_{(C,A)}^\circ = 0 \quad (19)$$

where $K_{(i,j)}$ and $\Delta G_{(i,j)}^\circ$, respectively, are the equilibrium constant and Gibbs free energy for ion exchange involving cations i and j . Note that $K_{(i,j)} = [K_{(j,i)}]^{-1}$ and $\Delta G_{(i,j)}^\circ = -\Delta G_{(j,i)}^\circ$.

Although the triangle rule can be used to predict the values of K and ΔG° for the third member of a set of three binary ion-exchange reactions, it is not possible to predict ion-exchange selectivity as a function of the zeolite composition (Townsend et al. 1984). Thus, it is essential to obtain isotherm data at one constant solution normality for each ion-exchange system of interest. With the data at one solution concentration, it would be possible to predict the ion-exchange isotherms over a large range of solution compositions and concentrations.

Systems that exhibit incomplete exchange

In some zeolites and for certain entering ions, A^{z_A+} , the exchange reactions reach a

⁶Equations (14) to (16) involve integrations from end-member compositions of the zeolite. However, data points near the extreme ends of ion-exchange isotherms can have large uncertainties (Laudelot 1987; Pabalan 1994), which can introduce significant errors in the results of the integration. An alternative approach to deriving ion-exchange thermodynamic parameters based on integrating isotherm data from two non-endmember compositions was recently presented by Ioannidis et al. (2000).

limit before all the B^{z_B+} ions initially present in the zeolite are replaced. Thus, it is not always possible to produce the homoionic A-zeolite, and it is necessary to ‘normalize’ the isotherm (Barrer et al. 1973). This procedure involves dividing all values of \bar{E}_A by the maximal value observed experimentally to give normalized values, i.e.

$$\bar{E}_A^N = \frac{\bar{E}_A}{\bar{E}_{A,\max.}} \quad (20)$$

This procedure does not affect the solution activity correction but does affect the calculation of the equilibrium constant and zeolite activity coefficients. A normalized Vanselow selectivity quotient, $K_{v(A,B)}^N$, is expressed in terms of the normalized cationic mole fractions, and the essential step in obtaining the thermodynamic equilibrium constant then involves evaluating (Barrer et al. 1973) the integral

$$\int_0^1 \ln K_{v(A,B)}^N d(\bar{E}_A^N) \quad (21)$$

Equations (14) to (16) are still applicable, but normalized parameters must be used throughout. For example, Equation (15) becomes

$$\ln f_A^{z_B} = -\bar{E}_B \ln K_{v(A,B)}^{N*} + \int_{\bar{E}_A^N}^1 \ln K_{v(A,B)}^N d(\bar{E}_A^N) \quad (22)$$

This procedure is necessary to conform to the definition of the exchanger phase standard state given previously. In effect, normalization results in the B^{z_B+} ions that are not involved in the exchange reaction being regarded as part of the exchanger framework (Dyer et al. 1981). These ions can still affect the ion-exchange equilibrium, but these effects are accounted for in f_A and f_B .

Townsend et al. (1984) noted that it is possible to apply the triangle rule successfully even in cases of partial ion exchange. However, they cautioned that great care must be exercised when applying the triangle rule to such systems because the standard states for all three exchange reactions must be consistent. As an example they noted that if data on ion exchange involving mordenite and Na^+/Cd^{2+} and Na^+/Pb^{2+} are used to predict $\Delta G_{(Cd,Pb)}^\circ$, a value of -11.44 kJ/mol is obtained, whereas if the NH_4^+/Cd^{2+} and NH_4^+/Pb^{2+} data are used, a predicted $\Delta G_{(Cd,Pb)}^\circ$ equal to 4.02 kJ/mol is obtained. The large difference arises from the difference in the values of $\bar{E}_{Cd,\max.}$ and $\bar{E}_{Pb,\max.}$. Townsend et al. (1984) concluded that *a priori* prediction of $\Delta G_{(A,B)}^\circ$ values when partial exchange occurs is inadvisable.

Activity coefficients of aqueous ions

It is apparent from the preceding equations that an evaluation of equilibrium constants and zeolite phase activity coefficients from experimental data involves activity correction for the aqueous phase. Ion-exchange studies by Fletcher and Townsend (1985) demonstrated the importance of correctly evaluating aqueous solution activity coefficients for accurate interpretation of exchange equilibria, particularly on systems with mixed background anions. In principle, γ 's, which account for nonideal behavior in the aqueous solution, can be calculated from well-established electrolyte solution theories (Bronsted 1922a,b; Guggenheim 1935; Scatchard 1936, 1968; Glueckauf 1949; Pitzer 1973, 1991). The ion-interaction model developed by Pitzer and coworkers was used to calculate the activity coefficients of aqueous ions for the examples presented in this chapter.⁷ This model has the advantage of having a large database of parameters at 298 K

⁷The ion-interaction model uses a molal (moles/kilogram H_2O) concentration scale, whereas the solution concentrations in this chapter are expressed in normality (equivalents/liter solution) or molarity (moles/liter solution).

and above, and it can be used for high ionic-strength aqueous solutions. The ion-interaction model has been used successfully in many applications to multicomponent systems over wide ranges of solution composition, concentration, and temperature.

For details on the ion-interaction model, the papers by Pitzer (1973, 1987, 1991) and the references cited therein should be consulted. The model gives expressions for single-ion activity coefficients, which are more convenient to use for complex mixed electrolytes than the use of mean activity coefficients and electrically neutral differences of activity coefficients (Pitzer 1991). However, it should be remembered that single-ion activity coefficients cannot be measured independently because of electroneutrality constraints. Ion-interaction parameters used in this study are listed in Table 2.

Table 2. Ion-interaction parameters used in this study to calculate aqueous activity coefficients using the Pitzer equations.*

<i>Single Electrolyte Parameters</i>			
Electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
NaCl	0.0765	0.2664	0.00127
KCl	0.04835	0.2122	-0.00084
CsCl	0.03478	0.03974	-0.000496
LiCl	0.1494	0.3074	0.00359
NH ₄ Cl	0.0522	0.1918	-0.00301
CaCl ₂	0.3159	1.614	-0.00034
SrCl ₂	0.2858	1.6673	-0.00130
NaNO ₃	0.0068	0.1783	-0.00072
KNO ₃	-0.0816	0.0494	0.00660
Ca(NO ₃) ₂	0.2108	1.409	-0.02014
<i>Mixture parameters</i>			
$\theta_{Na,K} = -0.012$	$\theta_{Na,Ca} = 0.07$	$\theta_{Na,Sr} = 0.051$	$\theta_{K,Sr} = 0.0149$
$\psi_{Na,K,Cl} = -0.0018$	$\psi_{Na,Ca,Cl} = -0.007$	$\psi_{Na,Sr,Cl} = -0.0021$	$\psi_{K,Sr,Cl} = -0.0201$
$\psi_{Na,K,NO_3} = -0.0012$	$\psi_{Na,Ca,NO_3} = -0.007$		
$\theta_{Na,Cs} = -0.03886$	$\theta_{K,Cs} = 0.0$	$\theta_{Na,Li} = 0.012$	$\theta_{K,Ca} = 0.032$
$\psi_{Na,Cs,Cl} = -0.00135$	$\psi_{K,Cs,Cl} = -0.0013$	$\psi_{Li,Na,Cl} = -0.003$	$\psi_{K,Ca,Cl} = -0.025$
$\theta_{Na,NH_4} = 0.004$	$\theta_{K,NH_4} = -0.065$		
$\psi_{Na,NH_4,Cl} = 0.0005$	$\psi_{K,NH_4,Cl} = 0.036$		

*Values were taken mostly from Pitzer (1991). ψ_{Na,Ca,NO_3} is based on the activity coefficient data of Smith et al. (1993). $\theta_{Na,Sr}$ and $\psi_{Na,Sr,Cl}$ are from Reardon and Armstrong (1987); $\theta_{K,Sr}$ and $\psi_{K,Sr,Cl}$ are from Kim and Frederick (1988); θ_{Na,NH_4} and $\psi_{Na,NH_4,Cl}$ are from Maeda et al. (1989); θ_{K,NH_4} and $\psi_{K,NH_4,Cl}$ are from Maeda et al. (1993).

For convenience, molal activity coefficients were not converted to a normal or molar basis. However, the errors contributed to the derived ion-exchange thermodynamic parameters or to the calculated isotherm values are small relative to errors introduced by analytical uncertainties (Pabalan 1994).

Activity coefficients of zeolite components

Various models have been proposed to represent the activity coefficients of exchangeable ions or solid solutions (Elprince and Babcock 1975; Elprince et al. 1980; Chu and Sposito 1981; Grant and Sparks 1989; Pabalan 1994; Morgan et al. 1995; Mehablia et al. 1996). Two models that have been used in ion-exchange studies are the Margules and Wilson equations. These equations have been widely applied to describe nonideal behavior in both solid and liquid solutions (Pitzer 1995).

Margules model. The Margules model has been used successfully in studies of ion-exchange equilibria involving zeolite minerals (Pabalan 1994; Shibue 1998). In this model, the molar excess Gibbs energy, \bar{G}^E , for a zeolite solid solution with two components, AL_{z_A} and BL_{z_B} , is represented by the equation

$$\frac{\bar{G}^E}{RT} = \bar{X}_A \bar{X}_B (\bar{X}_B W_A + \bar{X}_A W_B), \quad (23)$$

where W_A and W_B are empirical parameters that are functions only of temperature and pressure. From Equation (23) and the Gibbs-Duhem relation, the zeolite activity coefficients, f_A and f_B , can be expressed in terms of W_A and W_B as

$$\ln f_A = \bar{X}_B^2 [W_A + 2\bar{X}_A (W_B - W_A)]; \quad \ln f_B = \bar{X}_A^2 [W_B + 2\bar{X}_B (W_A - W_B)]. \quad (24)$$

Analogous expressions can be derived for solid solutions with three or more components (Grant and Sparks 1989; Mukhopadhyay et al. 1993).

The Vanselow selectivity coefficient, $K_{v(A,B)}$, can then be represented by

$$\ln K_{v(A,B)} = \ln K_{(A,B)} + z_A \bar{X}_A^2 [W_B + 2\bar{X}_B (W_A - W_B)] - z_B \bar{X}_B^2 [W_A + 2\bar{X}_A (W_B - W_A)]. \quad (25)$$

Values of $K_{(A,B)}$, W_A , and W_B can be derived by nonlinear regression of Equation (25) to isotherm data. If the zeolite phase behaves ideally, $f_A = f_B = 1$ and $\bar{G}^E = 0$ for all values of \bar{X}_A and \bar{X}_B , and $K_{(A,B)} = K_{v(A,B)}$. Values of W_A and W_B are zero for ideal solid solutions.

Wilson model. The Wilson model also has been applied successfully to studies of ion-exchange equilibria (e.g. Elprince and Babcock 1975; Shallcross et al. 1988; de Lucas et al. 1992; Mehablia et al. 1996; Shibue 1999; Ioannidis et al. 2000). The molar excess Gibbs energy for a two-component zeolite solid solution is taken to be

$$\frac{\bar{G}^E}{RT} = -\bar{X}_A \ln (\bar{X}_A + \Lambda_{AB} \bar{X}_B) - \bar{X}_B \ln (\bar{X}_B + \Lambda_{BA} \bar{X}_A), \quad (26)$$

where Λ_{AB} and Λ_{BA} are empirical parameters. The measure of nonideality in this model is the departure of the parameters from 1.0. For a solid solution that behaves ideally, $\Lambda_{AB} = \Lambda_{BA} = 1.0$. The corresponding activity coefficients for the binary solid solution are

$$\ln f_A = -\ln (\bar{X}_A + \Lambda_{AB} \bar{X}_B) + \bar{X}_B \left(\frac{\Lambda_{AB}}{\bar{X}_A + \Lambda_{AB} \bar{X}_B} - \frac{\Lambda_{BA}}{\bar{X}_B + \Lambda_{BA} \bar{X}_A} \right) \quad (27a)$$

and

$$\ln f_B = -\ln (\bar{X}_B + \Lambda_{BA} \bar{X}_A) + \bar{X}_A \left(\frac{\Lambda_{BA}}{\bar{X}_B + \Lambda_{BA} \bar{X}_A} - \frac{\Lambda_{AB}}{\bar{X}_A + \Lambda_{AB} \bar{X}_B} \right) \quad (27b)$$

The Wilson equation for multicomponent systems can be generalized to

$$\frac{\bar{G}^E}{RT} = -\sum_{i=1}^m \bar{X}_i \ln \left(\sum_{j=1}^m \Lambda_{ij} \bar{X}_j \right) \quad (28)$$

and the activity coefficient, f_k , of zeolite component k is given by

$$\ln f_k = 1 - \ln \left(\sum_{j=1}^m \Lambda_{kj} \bar{X}_j \right) - \sum_{i=1}^m \left(\frac{\Lambda_{ik} \bar{X}_i}{\sum_{j=1}^m \Lambda_{ij} \bar{X}_j} \right), \quad (29)$$

where Λ_{ii} , Λ_{jj} , Λ_{kk} , etc. are equal to 1.0 and the other Λ_{ij} are just the binary parameters. The absence of parameters beyond the binary terms makes the Wilson model attractive for application to ternary or more complex mixtures. However, Pitzer (1995) pointed out that interactions of three different species in a mixture do occur, and a provision for their representation is needed when they are significant.

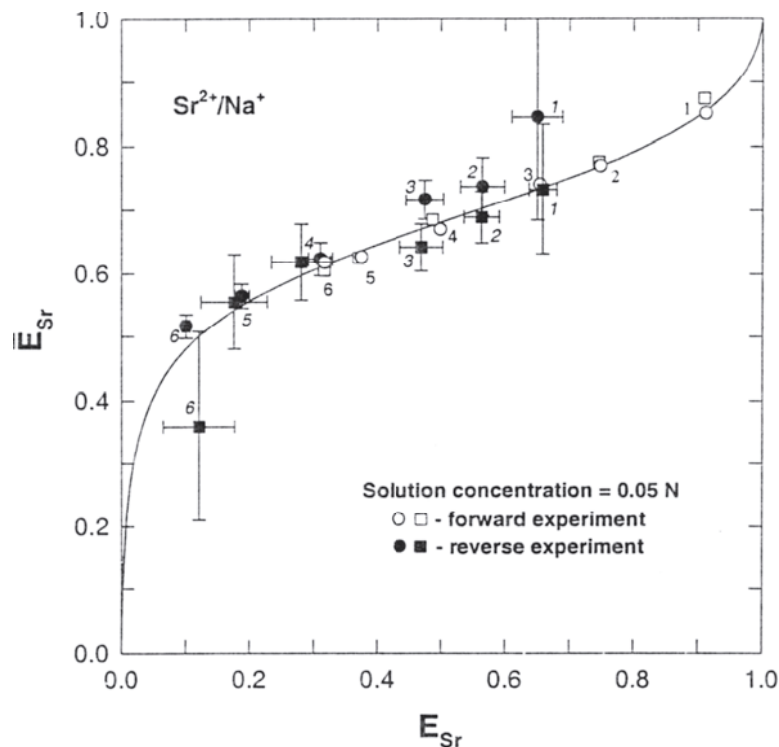


Figure 4. Isotherm data from forward and reverse $\text{Sr}^{2+}/\text{Na}^+$ experiments on clinoptilolite at 0.05 N solution concentration. Circles and squares were calculated from solution concentrations of Sr^{2+} and Na^+ data, respectively. The symbols are numbered to indicate matching forward and reverse data points. The curve is calculated using a Margules solid-solution model. Data from Pabalan and Bertetti (1999).

FACTORS TO CONSIDER IN EVALUATING ION-EXCHANGE DATA

Before ion-exchange experimental data can be subjected to thermodynamic treatment, it is important that the exchange reaction be shown to be reversible. An example of demonstrated reversibility is shown in Figure 4 for ion exchange involving clinoptilolite and $\text{Sr}^{2+}/\text{Na}^+$ solutions. However, most ion-exchange studies do not present data on reversibility.

The thermodynamic models used in evaluating exchanger phase activity coefficients essentially involve integrating Gibbs-Duhem type equations. The precision of parameters

derived from such models relies on the acquisition of accurate experimental data, particularly at the extreme ends of the isotherm plot. Small errors in the analysis of low concentrations of an ion can have a dramatic effect on the shapes of plots of the quantity $\ln K_{v(A,B)}$ versus composition. This is likely a primary explanation for the many discrepant results in the literature for a given system (Townsend 1986).

Other factors also cause discrepant data being obtained for different studies on a given exchange.⁸ It was common practice in past binary exchange measurements to analyze for the concentration of one ion only and to infer the concentration of the other ion by differences. However, for some zeolites hydronium exchange also takes place concomitantly with the other exchange reaction (Drummond et al. 1983). When this occurs, the exchange becomes a ternary exchange process and serious errors may result in the calculation of selectivity coefficients, especially at the extreme ends of isotherms.

A similar problem may occur for systems that exhibit incomplete exchange relative to a certain cation. During the course of an experiment the cation remaining in the solid phase may eventually exchange out, changing the nature of the exchange to a ternary reaction. For example, in Townsend and Loizidou's (1984) study on $\text{Na}^+/\text{NH}_4^+$ equilibria, clinoptilolite that had already been maximally exchanged for Na^+ released traces of K^+ when equilibrated with the mixed $\text{Na}^+/\text{NH}_4^+$ solutions. Thus, a third component was added to the exchange reaction. The K^+ concentration was low enough in this particular case that the reaction remained essentially binary (Townsend and Loizidou 1984).

Another potential source of error in ion-exchange experiments is dissolution of the zeolite framework. Zeolites and other aluminosilicates are not very resistant to strong acids and bases. Under acidic conditions, aluminum is preferentially dissolved, whereas silicon is preferentially dissolved in alkaline solutions. However, under neutral pH conditions, dissolution of aluminum and silicon is at a minimum and the effect of zeolite dissolution on ion-exchange equilibria usually can be neglected.

Therefore, in careful studies of ion-exchange equilibria, it is advisable to analyze for each exchanging ion in both the aqueous solution phase and the solid phase. This may be supplemented by analysis of other cations for systems that exhibit incomplete exchange or for systems in which more than two cations appear to participate in the exchange reactions. In cases where there is potential dissolution of the solid, aluminum and silicon concentrations in the aqueous phase may be analyzed to determine the extent of dissolution. The pH of the aqueous solution may also be controlled or monitored and other analytical techniques may be used. For example, scanning electron microscopy may be used to detect any visible evidence of mineral dissolution, and a more sophisticated technique such as ^{27}Al solid-state magic-angle spinning nuclear magnetic resonance spectroscopy may be used to characterize the aluminum sites in the zeolite structure.

Ion exchange studies on some natural zeolites, such as clinoptilolites, present special problems. Clinoptilolite minerals used in ion-exchange experiments are usually zeolitized volcanic tuff specimens. These commonly contain mineral impurities such as quartz, feldspar, smectite, and unaltered volcanic glass, and in some cases, other zeolites, halite, and calcite. Soluble salts and carbonate minerals, if not eliminated before conducting the experiments, can later dissolve and invalidate the assumption of binary exchange. In addition, thermodynamic treatment requires that the CEC be known. Previous studies have estimated the CEC from the Al^{3+} concentration in the zeolite determined by chemical analysis (e.g. Townsend and Loizidou 1984), from the concentration of

⁸Lehto and Harjula (1995) provided an excellent discussion of experimental factors that require careful consideration in order to obtain reliable and consistent ion-exchange results.

exchangeable cation(s) in the zeolite determined by chemical analysis (e.g. Barrer and Townsend 1976b), or from the observed maximum levels of exchange (e.g. Ames 1964a,b). Each of these methods has drawbacks caused by impurities in clinoptilolite samples. If the first method is used, chemical analysis of clinoptilolite will overestimate CEC in cases where feldspars or other aluminosilicate minerals are present and result in higher Al^{3+} content. If the second method is used, chemical analysis will overestimate the amount of exchangeable cations Na^+ , Mg^{2+} , and Ca^{2+} , hence CEC, in cases where impurities such as halite or carbonate minerals are present. On the other hand, CECs determined by the third method are sensitive to the method of pretreatment used (Semmens and Seyfarth 1978).

These problems can be minimized by careful characterization (e.g. analysis of mineralogical composition) or pretreatment (e.g. dissolution of soluble minerals or physical separation/purification) of zeolite specimens. Unfortunately, little attention has been given in many ion-exchange studies to the methods used in the preparation of the materials, or, in some cases, to their mineralogical and chemical composition. Thus, comparisons of experimental results and related thermodynamic quantities derived by various investigators can be complicated and, in more than a few cases, not very useful.

ION-EXCHANGE STUDIES ON NATURAL ZEOLITES

Literature information on the ion-exchange properties of the more common natural zeolites is summarized in this section. Information on a few synthetic zeolites, notably synthetic mordenite, is included for comparison. Equilibrium constants and Gibbs free energies taken from the literature are listed in tables. However, as noted previously, caution should be used when comparing published thermodynamic values because of the different materials (e.g. degrees of impurity, preparation method) used in the experiments, different temperatures, and different methods for calculating activity coefficients of aqueous cations. In most cases, the quality of the experimental data and the derived thermodynamic parameters have not been evaluated for this review. The original references should be consulted for details on experimental and analytical procedures and zeolite characterization.

Chabazite [$\text{Ca}_2(\text{Al}_4\text{Si}_8\text{O}_{24}) \cdot 12\text{H}_2\text{O}$]⁹

Chabazite was one of the first zeolites to be studied for its ion-exchange properties. Ames (1961) used a column apparatus to load natural zeolite samples with Cs^+ and competing cations to determine selectivity of the zeolites and to gain insight into the mechanisms responsible for a particular selectivity sequence. Natural chabazite crystals from Nova Scotia, Canada, hand-picked to greater than 95% purity, were exposed to solutions with a total concentration of 0.01 N at 298 K. Ames' results indicated a selectivity sequence of $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ for alkali metals and $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ for alkaline earths.

In extensive follow-up studies on the ion exchange of alkali metal cations and alkaline-earth cations in zeolites, Ames (1964a,b) conducted experiments on AW-500, a commercially available Na-form prepared from natural chabazite from a deposit near Bowie, Arizona. The CEC of the chabazite was determined to be 2.2 meq/g. Ion-exchange experiments were conducted at 298 and 343 K with a total solution normality of 1.0 N. Isotherms are presented in Ames (1964a) for the K^+/Na^+ system. Equilibrium constants and Gibbs free energy were determined for K^+/Cs^+ , K^+/Na^+ , Na^+/Cs^+ , $\text{Na}^+/\text{Sr}^{2+}$, $\text{Na}^+/\text{Ca}^{2+}$, and $\text{Ca}^{2+}/\text{Sr}^{2+}$ systems (Ames 1964a,b). The values are listed in Table 3.

⁹The idealized formula listed with the zeolite name is taken from Gottardi and Galli (1985).

Table 3. Literature values of equilibrium constants and Gibbs free energies for ion-exchange reactions involving chabazite

<i>Ion-Exchange Reaction</i>	<i>ln K_(A,B)</i>	$\Delta G_{(A,B)}^{\circ}$ (kJ/mol)*	<i>Reference</i>	<i>Remarks</i>
$\text{Li}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{LiL}$	-2.91	7.20	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{Na}^+ + \text{KL} \rightleftharpoons \text{K}^+ + \text{NaL}$	-1.98	4.91	Ames (1964a)	T=298 K; AW-500; Bowie, Arizona chabazite
$\text{K}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{KL}$	2.70	-6.69	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{K}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{KL}$	2.1	-5.2	Torracca et al. (1998)	T = 298 K; Avellino, Italy chabazite; normalized isotherm
$\text{Rb}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{RbL}$	2.26	-5.61	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{Cs}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{CsL}$	3.93	-9.7	Perona (1993)	T = 296 K; Ionsiv
$\text{Cs}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{CsL}$	3.39	-8.40	Ames (1964a)	T=298 K; AW-500; Bowie, Arizona chabazite
$\text{Cs}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{CsL}$	4.22	-10.46	Barrer et al. (1969)	T = 298 K; ; Nova Scotia, Canada chabazite; normalized isotherm
$\text{Cs}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{CsL}$	4.56; 4.27; 3.90	-11.3; -11.1; -10.8	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Cs}^+ + \text{NaL} \rightleftharpoons \text{Na}^+ + \text{CsL}$	2.59	-7.39	Ames (1964a)	T=343 K; AW-500; Bowie, Arizona chabazite
$\text{Cs}^+ + \text{KL} \rightleftharpoons \text{K}^+ + \text{CsL}$	2.8; 2.7; 2.7	-6.9; -6.9; -7.4	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Cs}^+ + \text{KL} \rightleftharpoons \text{K}^+ + \text{CsL}$	1.49	-3.69	Ames (1964a)	T=298 K; AW-500; Bowie, Arizona chabazite
$\text{Cs}^+ + \text{KL} \rightleftharpoons \text{K}^+ + \text{CsL}$	1.49	-4.25	Ames (1964a)	T=343 K; AW-500; Bowie, Arizona chabazite
$\text{Cs}^+ + \text{RbL} \rightleftharpoons \text{Rb}^+ + \text{CsL}$	1.8; 1.8; 1.7	-4.5; -4.8; -4.8	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Cs}^+ + 0.5\text{MgL}_2 \rightleftharpoons \text{Mg}^{2+} + \text{CsL}$	6.78; 5.73; 5.67	-16.8; -14.9; -15.7	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Cs}^+ + 0.5\text{CaL}_2 \rightleftharpoons 0.5\text{Ca}^{2+} + \text{CsL}$	5.17; 5.03; 4.88	-12.8; -13.1; -13.5	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite

$\text{Cs}^+ + 0.5\text{BaL} \Leftrightarrow 0.5\text{Ba}^{2+} + \text{CsL}$	4.52; 4.30; 4.12	-11.2; -11.2; -11.4	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$\text{Cs}^+ + 0.5\text{SrL}_2 \Leftrightarrow 0.5\text{Sr}^{2+} + \text{CsL}$	5.81; 5.80; 5.49	-14.4; -15.1; -15.2	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$\text{NH}_4^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{NH}_4\text{L}$	2.5	-6.1	Torracca et al. (1998)	T = 298 K; Avellino, Italy chabazite; normalized isotherm
$\text{NH}_4^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{NH}_4\text{L}$	1.67	-4.14	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{Ag}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{AgL}$	2.43	-6.02	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{TI}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{TIL}$	4.42	-10.96	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{Mg}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{MgL}_2$	-7.6	19	Perona (1993)	T = 296 K; Ionsiv
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	-3.82	9.46	Perona (1993)	T = 296 K; Ionsiv
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	-0.323	0.800	Ames (1964b)	T=298 K; AW-500; Bowie, Arizona chabazite
$0.5\text{Ca}^{2+} + \text{NaL} \Leftrightarrow \text{Na}^+ + 0.5\text{CaL}_2$	0.08; 0.12; 0.22	-0.2; -0.3; -0.6	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	-0.3	0.75	Barrer et al. (1969)	T = 323 K; Nova Scotia, Canada chabazite
$0.5\text{Ca}^{2+} + \text{KL} \Leftrightarrow \text{K}^+ + 0.5\text{CaL}_2$	-1.3; -1.1; -0.94	3.3; 2.9; 2.6	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$0.5\text{Ca}^{2+} + \text{RbL} \Leftrightarrow \text{Rb}^+ + 0.5\text{CaL}_2$	-1.7; -1.5; -1.4	4.3; 4.0; 3.9	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$0.5\text{Ca}^{2+} + \text{CsL} \Leftrightarrow \text{Cs}^+ + 0.5\text{CaL}_2$	-2.1; -1.9; -1.7	5.2; 5.0; 4.6	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$\text{Ca}^{2+} + \text{MgL}_2 \Leftrightarrow \text{Mg}^{2+} + \text{CaL}_2$	1.3; 1.2; 1.3	-3.2; -3.2; -3.5	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$\text{Ca}^{2+} + \text{SrL}_2 \Leftrightarrow \text{Sr}^{2+} + \text{CaL}_2$	0.57; 0.61; 0.61	-1.4; -1.6; -1.7	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$\text{Ca}^{2+} + \text{BaL}_2 \Leftrightarrow \text{Ba}^{2+} + \text{CaL}_2$	0.32; 0.35; 0.36	-0.8; -0.9; -1.0	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite
$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-1.84	4.56	Perona (1993)	T = 296 K; Ionsiv
$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-1.24	3.07	Ames (1964b)	T=298 K; AW-500 (Bowie, Arizona) chabazite
$0.5\text{Sr}^{2+} + \text{NaL} \Leftrightarrow \text{Na}^+ + 0.5\text{SrL}_2$	0.04; 0.19; 0.22	-0.1; -0.5; -0.6	Dyer and Zubair (1998)	T = 298 K; 313 K; 333 K; Bowie, Arizona chabazite

$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-0.13	0.33	Barrer et al. (1969)	Bowie, Arizona chabazite T = 323 K; Nova Scotia, Canada chabazite
$0.5\text{Sr}^{2+} + \text{KL} \Leftrightarrow \text{K}^+ + 0.5\text{SrL}_2$	-1.4; -1.2; -1.1	3.4; 3.1; 3.1	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$0.5\text{Sr}^{2+} + \text{RbL} \Leftrightarrow \text{Rb}^+ + 0.5\text{SrL}_2$	-1.9; -1.7; -1.5	4.8; 4.3; 4.1	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$0.5\text{Sr}^{2+} + \text{CsL} \Leftrightarrow \text{Cs}^+ + 0.5\text{SrL}_2$	-2.4; -1.9; -1.6	5.9; 4.9; 4.4	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Sr}^{2+} + \text{MgL}_2 \Leftrightarrow \text{Mg}^{2+} + \text{SrL}_2$	-4.24; -4.07; -4.08	10.5; 10.6; 11.3	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Sr}^{2+} + \text{CaL}_2 \Leftrightarrow \text{Ca}^{2+} + \text{SrL}_2$	-2.2; -2.1; -2.0	5.4; 5.4; 5.4	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Sr}^{2+} + \text{CaL} \Leftrightarrow \text{Ca}^+ + \text{SrL}_2$	-0.992	2.46	Ames (1964b)	T=298 K; AW-500; Bowie, Arizona chabazite
$\text{Sr}^{2+} + \text{BaL}_2 \Leftrightarrow \text{Ba}^{2+} + \text{SrL}_2$	0.08; 0.15; 0.18	-0.2; -0.4; -0.5	Dyer and Zubair (1998)	T = 298 K; 313 K; 333K; Bowie, Arizona chabazite
$\text{Ba}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{BaL}_2$	0.0	0.00	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{Pb}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{PbL}_2$	1.4	-3.4	Torracca et al. (1998)	T = 298 K; Avellino, Italy chabazite
$\text{Pb}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{PbL}_2$	0.57	-1.42	Barrer et al. (1969)	T = 298 K; Nova Scotia, Canada chabazite
$\text{Cu}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CuL}_2$	-2.5	6.1	Colella et al. (1998)	T = 298K; Riano, Italy chabazite; normalized isotherm
$\text{Zn}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{ZnL}_2$	-3.3	8.2	Colella et al. (1998)	T = 298K; Riano, Italy chabazite; normalized isotherm

*Values from Barrer et al. (1969), given in kilocalories per equivalent, were converted to kilojoules per mole.

Barrer et al. (1969) studied the exchange of a variety of cations with Na^+ in a natural chabazite from Nova Scotia, Canada. Na-chabazite was prepared by repeated exchange of the natural material with NaCl solutions. The CEC for the Na-chabazite was calculated to be 3.49 meq/g. Experiments were conducted at 298 K, except for exchanges of Sr^{2+} and Ca^{2+} for Na^+ , which were conducted at 323 K. Cs^+ exhibited incomplete exchange with Na^+ , reaching only 0.84 of the CEC ($\bar{E}_{\text{Cs,max.}} = 0.84$). Isotherms for all experiments conducted are presented in the paper. A general selectivity sequence, based on the standard free energies of exchange, is given as $\text{Ti}^+ > \text{K}^+ > \text{Ag}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{Pb}^{2+} > \text{Na}^+ = \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Li}^+$. Heats of exchange were also determined by calorimetry. Gibbs free energy values determined by Barrer et al. (1969) and equilibrium constants derived from those values are listed in Table 3.

Dyer and Zubair (1998) produced ion-exchange isotherms for several homoionic forms of a purified natural chabazite from a deposit near Bowie, Arizona. K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} were exchanged with radiolabeled Cs^+ , Sr^{2+} , and Ca^{2+} in solutions of 0.01 N concentration at temperatures of 298, 313, and 333 K. The authors reported that reversible ion exchange was exhibited in all cases¹⁰ and temperature had little effect on the nature of the isotherms. Some slight differences in thermodynamic values were attributed to differences in the Si/Al ratio of the chabazites used for the study. The derived thermodynamic values are very similar to those from previous studies. Thermodynamic data from Dyer and Zubair (1998) are listed in Table 3.

The potential to remove Pb^{2+} from wastewaters through ion exchange in natural chabazite, obtained from San Mango sul Calore, Italy, was investigated by Colella and Pansini (1988). The mean value of CEC for the chabazite used in their study was 1.70 meq/g. The authors concluded that chabazite was selective for Pb^{2+} , but high concentrations of Na^+ interfered with exchange.

Colella et al. (1998) investigated the exchange of Cu^{2+} and Zn^{2+} with Na^+ using purified chabazite obtained from chabazite-rich tuff near Riano, Italy. The purified chabazite was converted to a Na-form through exchange with NaCl solution. The measured CEC of the chabazite was 3.37 meq/g. Isotherms were generated from experiments conducted at 298 K in solutions of Cu^{2+} , Zn^{2+} , and Na^+ at a total concentration of 0.1 N (NO_3^- co-anion). Results for $\text{Cu}^{2+}/\text{Na}^+$ and $\text{Zn}^{2+}/\text{Na}^+$ exchange indicated that the ion-exchange reactions were reversible. However, exchange was not complete for Zn^{2+} , with an $\bar{E}_{\text{Zn,max.}}$ equal to 0.83. Thermodynamic values determined by Colella et al. (1998) are given in Table 3.

Torracca et al. (1998) studied the ion exchange of Na^+ with Pb^{2+} , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} . Torracca et al. (1998) used chabazite prepared from a chabazite-rich tuff outcrop near Avellino, Italy. The chabazite was purified and converted to the Na-form through contact with NaCl solutions. The CEC for the chabazite was determined to be 2.75 meq/g. Isotherms were produced through experiments conducted at 0.1 N solution concentration and 298 K. Exchange kinetics were slow for Ca^{2+} and Mg^{2+} , an observation that agrees with results from previous studies (Barrer et al. 1969). Although the ion-

¹⁰ However, the reported reversibility of the ion-exchange reactions is not consistent with some of the tabulated Gibbs free energies of ion exchange. The Gibbs free energies for three reverse reactions: (1) $2\text{CsL} \rightarrow \text{SrL}_2$ and $\text{SrL}_2 \rightarrow 2\text{CsL}$, (2) $2\text{CsL} \rightarrow \text{CaL}_2$ and $\text{CaL}_2 \rightarrow 2\text{CsL}$, and (3) $\text{CaL}_2 \rightarrow \text{SrL}_2$ and $\text{SrL}_2 \rightarrow \text{CaL}_2$, do not sum to zero and, instead, sum to several kilojoules per mole. Dyer suggested (personal communication with A. Dyer, August 9, 2000) that multication exchange may have occurred, possibly because (1) none of the samples is truly homoionic such that Na^+ impurity may have played a role, and (2) the hydronium ion usually plays a role in zeolite ion exchange.

exchange reactions were reversible, incomplete exchange was observed for Na^+/K^+ and $\text{Na}^+/\text{NH}_4^+$. A selectivity sequence of $\text{NH}_4^+ > \text{K}^+ > \text{Pb}^{2+} > \text{Na}^+$ was determined. Thermodynamic quantities for $\text{Na}^+/\text{NH}_4^+$, Na^+/K^+ , and $\text{Na}^+/\text{Pb}^{2+}$ systems as determined by Torracca et al. (1998) are provided in Table 3.

Chabazite has been used at Oak Ridge National Laboratory to clean up various waste streams containing radioactive Sr^{2+} and Cs^+ (Robinson et al. 1991; Perona 1993; Robinson et al. 1995; DePaoli and Perona 1996). Perona (1993) modeled isotherm data to derive thermodynamic parameters for $\text{Na}^+/\text{Sr}^{2+}$, Na^+/Cs^+ , $\text{Na}^+/\text{Ca}^{2+}$, and $\text{Na}^+/\text{Mg}^{2+}$ ion exchange. The data were based on experiments using a Na-exchanged natural chabazite from a deposit near Bowie, Arizona (commercially available from Ionsiv), conducted at 296 K and solution concentrations of 0.01 N or below. Perona (1993) extended the binary system data to model a five-component system. Values of the ion-exchange equilibrium constants derived by Perona (1993) and the associated Gibbs free energies are listed in Table 3.

Clinoptilolite [(Na,K)₆(Al₆Si₃₀O₇₂)·20H₂O]

Numerous ion-exchange studies have been performed on clinoptilolite, primarily because of its ability to extract ^{137}Cs from radioactive waste solutions and the NH_4^+ ion from municipal wastewater streams. The earliest comprehensive investigations into the selectivity of clinoptilolite for inorganic ions were conducted by Ames (1960, 1961) using column experiments and clinoptilolite from Hector, California. These studies demonstrated the high selectivity of clinoptilolite for Cs^+ and established the selectivity series $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ for the alkali elements, and $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ for the alkaline-earth elements, on the basis of the power of the different cations to compete with Cs^+ . Other studies during that period evaluated the use of clinoptilolite in extracting ^{137}Cs and ^{90}Sr from radioactive wastes (Mercer 1960; Nelson et al. 1960; Mathers and Watson 1962; Tomlinson 1962). Because clinoptilolite also exhibits relatively high selectivity for NH_4^+ , some studies evaluated its use in the treatment of municipal wastewater (Mercer 1966; Ames 1967; Mercer et al. 1970).

Semmens and Seyfarth (1978) published isotherm data on ion exchange between Na-clinoptilolite, prepared using zeolite material from Buckhorn New Mexico, and the heavy metal ions Ba^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} . They reported good reversibilities for the exchange couples $\text{Na}^+/\text{Ba}^{2+}$, $\text{Na}^+/\text{Cd}^{2+}$, and $\text{Na}^+/\text{Cu}^{2+}$, but not for $\text{Na}^+/\text{Pb}^{2+}$ and $\text{Na}^+/\text{Zn}^{2+}$. They showed that heavy metals are concentrated well by clinoptilolite at low solution fractions of the heavy metals ($E_A < 0.1$), and they established the selectivity sequence $\text{Pb}^{2+} \approx \text{Ba}^{2+} \gg \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+} > \text{Na}^+$. The reported isotherms were not complete, i.e. isotherm points were derived to heavy-metal solution fractions typically < 0.6 . Therefore, it is not possible to tell from the data whether full exchange between Na-clinoptilolite and the heavy metals could be achieved. The isotherm curves for barium and cadmium exchange level off at $E_A \approx 0.6\text{--}0.8$, suggesting partial exchange for the $\text{Na}^+/\text{Ba}^{2+}$ and $\text{Na}^+/\text{Cd}^{2+}$ couples.

Also, the results of Semmens and Seyfarth (1978) indicated that the ion-exchange capacity of clinoptilolite depends significantly on the method used to pretreat the samples. For example, the ion-exchange capacity, determined from the amount of NH_4^+ eluted from the NH_4 -form of the clinoptilolite by exchange with NaCl solution, tends to increase with repeated capacity determinations on the same zeolite sample. This result has important implications on the manner in which ion-exchange experiments on clinoptilolite are conducted if reproducible results are to be achieved and if valid extrapolation of experimental data to other clinoptilolite samples is desired.

Blanchard et al. (1984) conducted batch experiments to study the removal of NH_4^+ and heavy metals from waters by Na-clinoptilolite. The results show that clinoptilolite has a good selectivity for the NH_4^+ ion. Based on the isotherm data, they determined the selectivity series $\text{Pb}^{2+} > \text{NH}_4^+, \text{Ba}^{2+} > \text{Cu}^{2+}, \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+}$.

Zamzow et al. (1990) conducted column experiments and measured the ion-exchange loading of heavy metals and other cations on clinoptilolite material from Owyhee County, Idaho, and from Ash Meadows, Nevada. The clinoptilolite samples were primarily in the Na- or Ca-form, but potassium and magnesium were also present in the zeolite. The loading tests were done by passing one liter of a 0.1 M solution of the cation of interest through a 30-cm long by 1-cm diameter glass column containing the zeolite powder. The measured heavy metal loading values, which ranged from 0 meq/g for mercury and 1.6 meq/g for lead, were used to determine the following selectivity series: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cs}^+ > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$.

In addition to column experiments, Ames (1964a,b) also conducted batch experiments on clinoptilolite and alkali and alkaline-earth cations and presented ion-exchange isotherms for the couples Cs^+/K^+ , Na^+/K^+ , Cs^+/Na^+ , $\text{Ca}^{2+}/\text{Na}^+$, $\text{Sr}^{2+}/\text{Na}^+$, and $\text{Sr}^{2+}/\text{Ca}^{2+}$. The ion-exchange equilibrium constants and Gibbs free energies derived by Ames (1964a,b) from the isotherm data are listed in Table 4. Additional thermodynamic values reported by Ames (1968) for Cs^+/K^+ and Cs^+/Na^+ exchange are also listed in the table. Other early studies on clinoptilolite ion exchange were reported by Frysinger (1962) for Na^+/Cs^+ , and by Howery and Thomas (1965) for the binary mixtures of Na^+/Cs^+ , $\text{Na}^+/\text{NH}_4^+$, and $\text{NH}_4^+/\text{Cs}^+$. The results of Frysinger (1962) demonstrated that clinoptilolite is selective for Cs^+ relative to Na^+ , whereas Howery and Thomas (1965) noted a selectivity sequence for clinoptilolite of $\text{Cs}^+ > \text{NH}_4^+ \gg \text{Na}^+$. The equilibrium constants and Gibbs free energies reported by Frysinger (1962) and Howery and Thomas (1965) are included in Table 4.

Chelishchev et al. (1973) presented isotherm data for ion exchange involving clinoptilolite and mixtures of Na^+/Cs^+ , Na^+/Rb^+ , Na^+/K^+ , Na^+/Li^+ , and $\text{Na}^+/\text{Sr}^{2+}$. Their results show that the exchange reactions are all reversible, and the selectivity series is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Sr}^{2+} > \text{Li}^+$. Thermodynamic data derived from their isotherm data are listed in Table 4.

Townsend and co-workers conducted a number of ion-exchange studies using clinoptilolite samples from Hector, California. Barrer and Townsend (1976b) studied the exchange equilibria between the NH_4^+ -form of clinoptilolite and copper ammine and zinc ammine metal complexes. The exchange isotherms indicated maximum exchange limits of 88% and 73% for the copper and zinc, respectively. Reversibility tests showed good reversibility for the copper ammine + clinoptilolite system, but not for zinc ammine + clinoptilolite. The method used to test for reversibility in the latter case involved drying the zeolite sample at 353 K before measuring the reverse isotherm points, and this apparently allowed the zinc ions to enter exchange sites not accessible to the complexed species at ambient temperatures (Barrer and Townsend 1976b). Thus the reverse isotherm points were at higher values of \bar{E}_{Zn} than for the forward isotherm points. The results of Barrer and Townsend (1976b) also showed that ammination improves the selectivity of clinoptilolite for copper and zinc, and that the zeolite shows increasing selectivity for the complexed transition metal ion with decreasing concentration. Values of equilibrium constants and Gibbs free energy of exchange were not calculated by the authors because the activity coefficients of the complexed ions in solution were not known and partly because the systems exhibited incomplete exchange (Barrer and Townsend 1976b).

Townsend and Loizidou (1984) published an isotherm for $\text{Na}^+/\text{NH}_4^+$ exchange in

Table 4. Literature values of equilibrium constants and Gibbs free energies for ion-exchange reactions involving clinoptilolite.

Ion-Exchange Reaction	$\ln K_{(A,B)}$	$\Delta G_{(A,B)}^\circ$ (kJ/mol)	Reference	Remarks
$\text{Li}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{LiL}$	-2.34	5.74	Chelishchev et al. (1973)	T = 295 K
$\text{Na}^+ + \text{CsL} \Leftrightarrow \text{Cs}^+ + \text{NaL}$	-3.15	8.46	Frysinger (1962)	T = 323 K
$\text{Na}^+ + \text{CsL} \Leftrightarrow \text{Cs}^+ + \text{NaL}$	-2.58	7.47	Frysinger (1962)	T = 348 K
$\text{Na}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{NaL}$	-2.54	6.29	Ames (1964a)	T = 298 K; Hector, California clinoptilolite; CEC = 1.7 meq/g
$\text{K}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{KL}$	3.22	-7.98	Pabalan (1994)	T = 298 K; Death Valley Junction, California clinoptilolite; CEC = 2.04 meq/g; aqueous activity coefficients calculated using the Pitzer equations
$\text{K}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{KL}$	3.68	-9.03	Chelishchev et al. (1973)	T = 295 K
$2\text{K}^+ + \text{CaL}_2 \Leftrightarrow \text{Ca}^{2+} + 2\text{KL}$	2.22	-5.50	Vucinic (1998a)	T = 298 K; Serbia clinoptilolite; incomplete exchange of Ca^{2+} by NH_4^+ ; isotherm data normalized
$\text{Rb}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{RbL}$	3.91	-9.60	Chelishchev et al. (1973)	T = 295 K
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	4.14	-10.2	Chelishchev et al. (1973)	T = 295 K
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	3.28	-8.07	Ames (1968)	T = 296 K; Pierre clinoptilolite; CEC = 1.32 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	3.86	-9.56	Ames (1964a)	T = 298 K; John Day, Oregon clinoptilolite; CEC = 2.0 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	3.95	-9.79	Ames (1964a)	T = 298 K; Hector, California clinoptilolite; CEC = 1.7 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	4.02	-10.1	Howery and Thomas (1965)	T = 303K; CEC = 2.04±0.02 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	3.21	-9.16	Ames (1964a)	T = 343 K; John Day, Oregon clinoptilolite; CEC = 2.0 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	2.94	-8.38	Ames (1964a)	T = 343 K; Hector, California clinoptilolite; CEC = 1.7 meq/g
$\text{Cs}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{CsL}$	1.55	-3.81	Ames (1968)	T = 296 K; Hector, California clinoptilolite; CEC = 1.7 meq/g

$\text{Cs}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{CsL}$	1.30	-3.22	Ames (1964a)	T = 298 K; Hector, California clinoptilolite; CEC = 1.7 meq/g
$\text{Cs}^+ + \text{NH}_4\text{L} \Leftrightarrow \text{NH}_4^+ + \text{CsL}$	1.69	-4.27	Howery and Thomas (1965)	T = 303K; CEC = 2.04±0.01 meq/g
$\text{NH}_4^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{NH}_4\text{L}$	1.63	-4.04	Townsend and Loizidou (1984)	T = 298 K; Hector, California clinoptilolite; CEC = 2.19; isotherm data normalized to $\bar{E}_{\text{NH}_4, \text{max}}$ of 0.765
$\text{NH}_4^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{NH}_4\text{L}$	1.65	-4.09	Jama and Yucel (1990)	T = 298 K; Western Anatolia clinoptilolite; isotherm data normalized to $\bar{E}_{\text{NH}_4, \text{max}}$ of 0.68
$\text{NH}_4^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{NH}_4\text{L}$	2.14	-5.40	Howery and Thomas (1965)	T = 303K; CEC = 2.04±0.01 meq/g
$\text{NH}_4^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{NH}_4\text{L}$	2.07	-5.73	Barrer et al. (1967)	T = 333 K; Hector, California clinoptilolite; CEC = 1.83
$\text{NH}_4^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{NH}_4\text{L}$	-0.163	0.403	Jama and Yucel (1990)	T = 298 K; Western Anatolia clinoptilolite; isotherm data normalized to $\bar{E}_{\text{NH}_4, \text{max}}$ of 0.50
$2\text{NH}_4^+ + \text{CaL}_2 \Leftrightarrow \text{Ca}^{2+} + 2\text{NH}_4\text{L}$	4.98	-12.3	Jama and Yucel (1990)	T = 298 K; Western Anatolia clinoptilolite; isotherm data normalized to $\bar{E}_{\text{NH}_4, \text{max}}$ of 0.64
$2\text{NH}_4^+ + \text{CaL}_2 \Leftrightarrow \text{Ca}^{2+} + 2\text{NH}_4\text{L}$	4.868	-12.07	Vucinic (1998a)	T = 298 K; Serbia clinoptilolite; complete exchange reported, but used a lower CEC (1.5, instead of 2.1 meq/g) to calculate isotherms
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	-0.161	0.400	Ames (1964b)	T = 298 K; Hector, California clinoptilolite; CEC = 1.7 meq/g
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	-1.65	4.09	Pabalan (1994)	T = 298 K; Death Valley Junction, California clinoptilolite; CEC = 2.04 meq/g; aqueous activity coefficients calculated using the Pitzer equations
$\text{Ca}^{2+} + 2\text{KL} \Leftrightarrow 2\text{K}^+ + \text{CaL}_2$	-8.50	21.1	Pabalan and Bertetti (1999)	T = 298 K; Death Valley Junction, California clinoptilolite; CEC = 2.04 meq/g; aqueous activity coefficients

				calculated using the Pitzer equations
$\text{Sr}^{2+} + 2\text{NaL} \rightleftharpoons 2\text{Na}^+ + \text{SrL}_2$	1.19	-2.92	Chelishchev et al. (1973)	T = 295 K
$\text{Sr}^{2+} + 2\text{NaL} \rightleftharpoons 2\text{Na}^+ + \text{SrL}_2$	-1.14	2.83	Pabalan and Bertetti (1999)	T = 298 K; Death Valley Junction, California clinoptilolite; CEC = 2.04 meq/g; aqueous activity coefficients calculated using the Pitzer equations
$\text{Sr}^{2+} + 2\text{NaL} \rightleftharpoons 2\text{Na}^+ + \text{SrL}_2$	0.255	-0.632	Ames (1964b)	T = 298 K; Hector, California clinoptilolite; CEC = 1.7 meq/g
$\text{Sr}^{2+} + 2\text{KL} \rightleftharpoons 2\text{K}^+ + \text{SrL}_2$	-6.52	16.2	Pabalan and Bertetti (1999)	T = 298 K; Death Valley Junction, California clinoptilolite; CEC = 2.04 meq/g; aqueous activity coefficients calculated using the Pitzer equations
$\text{Sr}^{2+} + \text{CaL}_2 \rightleftharpoons \text{Ca}^{2+} + \text{SrL}_2$	0.113	-0.280	Ames (1964b)	T = 298 K; Hector, California clinoptilolite; CEC = 1.7 meq/g
$\text{Cd}^{2+} + 2\text{NaL} \rightleftharpoons 2\text{Na}^+ + \text{CdL}_2$	-2.23	5.53	Loizidou and Townsend (1987a)	T = 298 K; Hector, California clinoptilolite; CEC = 2.19; isotherm data normalized to $\bar{E}_{\text{Cd,max}}$ of 0.656; Cl^- co-anion
$\text{Cd}^{2+} + 2\text{NaL} \rightleftharpoons 2\text{Na}^+ + \text{CdL}_2$	-1.83	4.54	Loizidou and Townsend (1987a)	T = 298 K; Hector, California clinoptilolite; CEC = 2.19; isotherm data normalized to $\bar{E}_{\text{Cd,max}}$ of 0.656; NO_3^- co-anion
$\text{Cd}^{2+} + 2\text{NaL} \rightleftharpoons 2\text{Na}^+ + \text{CdL}_2$	0.388	-0.962	Torres (1999)	T = 298 K; CEC = 1.60 (measured); 1.92 (calculated); isotherm data not normalized
$\text{Pb}^{2+} + 2\text{NaL} \rightleftharpoons 2\text{Na}^+ + \text{PbL}_2$	3.085 (at 0.1 N) 3.215 (at 0.5 N)	-7.64 (at 0.1 N) -7.96 (at 0.5 N)	Loizidou and Townsend (1987b)	T = 298 K; Hector, California clinoptilolite; CEC = 2.19; isotherm data normalized to $\bar{E}_{\text{Pb,max}}$ of 0.795; NO_3^- co-anion

clinoptilolite and compared their derived thermodynamic constants with those determined by other workers. Their results showed that clinoptilolite exhibits a high preference for NH_4^+ over Na^+ . However, the exchange is incomplete, with $\bar{E}_{\text{NH}_4, \text{max}}$ equal to 0.765, indicating that the theoretical exchange capacity estimated from the chemical analysis of the zeolite cannot be attained with NH_4^+ . Townsend and Loizidou (1984) noted that the partial exchange of NH_4^+ for Na^+ observed in their experiment is in contrast to results of Howery and Thomas (1965), who observed full exchange of the Na^+ in their zeolite by NH_4^+ . However, Howery and Thomas (1965) did not publish their isotherm data. On the other hand, Barrer et al. (1967) observed full exchange of Na^+ by NH_4^+ in their experiments at a temperature of 333 K. The Gibbs free energy reported by Townsend and Loizidou (1984), listed in Table 4, is different from that of Howery and Thomas (1965). Townsend and Loizidou (1984) suggested that this difference could be due to the variability of the mineral samples.

Jama and Yucel (1990) published isotherm data on ion exchange involving clinoptilolite from Western Anatolia and mixtures of $\text{Na}^+/\text{NH}_4^+$, K^+/NH_4^+ , and $\text{Ca}^{2+}/\text{NH}_4^+$. The results showed that clinoptilolite exhibits very high preference for NH_4^+ over Na^+ and Ca^{2+} , but not over K^+ . Consistent with the results of Townsend and Loizidou (1984), Jama and Yucel (1990) observed that full replacement of the cations by NH_4^+ was not achieved, with $\bar{E}_{\text{NH}_4, \text{max}}$ equal to 0.68, 0.50, and 0.64 for Na-, K-, and Ca-clinoptilolite, respectively. Jama and Yucel (1990) also noted that the exchange reactions were not strictly binary, i.e. when the Na-, K-, or Ca-forms of clinoptilolite were reacted with the mixed cation/ammonium ion solutions, other cations (e.g. K^+ , Ca^{2+} , and Mg^{2+}) were also detected in solution. However, these other cations amounted to less than 5% of the total cation equivalents in solution. Equilibrium constants and Gibbs free energies reported by Jama and Yucel (1990) are listed in Table 4.

Data on ion exchange between clinoptilolite material from Serbia and aqueous mixtures of $\text{K}^+/\text{Ca}^{2+}$ and $\text{NH}_4^+/\text{Ca}^{2+}$ were presented by Vucinic (1998a). In contrast to the results of Jama and Yucel (1990) and Townsend and Loizidou (1984), Vucinic (1998a) reported that complete exchange was achieved between Ca^{2+} and NH_4^+ . However, Vucinic (1998a) used a CEC value of 1.50 meq/g to calculate the isotherm points, instead of 2.10, which is the CEC measured by the author from exchange with NH_4^+ and from the Al^{3+} content of the clinoptilolite. The author also reported that only partial exchange was achieved between Ca^{2+} and K^+ , with $\bar{E}_{\text{K}, \text{max}}$ of about 0.68, which is inconsistent with the complete exchange observed by Pabalan and Bertetti (1999). Equilibrium constants and Gibbs free energies reported by Vucinic (1998a) for a temperature of 298 K are listed in Table 4.

Isotherms for the exchange of Cd^{2+} into the Na- and NH_4 -forms of clinoptilolite were published by Loizidou and Townsend (1987a) based on experiments using chloride or nitrate as the co-anion. Their results indicate that the ion-exchange reaction is reversible for the $\text{Cd}^{2+}/\text{Na}^+$ couple, but not for the $\text{Cd}^{2+}/\text{NH}_4^+$ couple. Only partial exchange was observed for the two couples, with $\bar{E}_{\text{Cd}, \text{max}}$ equal to 0.656 for the $\text{Cd}^{2+}/\text{Na}^+$ exchange and 0.810 for the $\text{Cd}^{2+}/\text{NH}_4^+$ reaction. Also, clinoptilolite was observed to be more selective for cadmium when nitrate is the co-anion rather than chloride. The observed effect of co-anion type on selectivity was attributed to the tendency of cadmium to form aqueous complexes with the chloride ion. The observed incomplete exchange for the $\text{Cd}^{2+}/\text{Na}^+$ couple is consistent with more recent data from Torres (1999). Thermodynamic data for the $\text{Cd}^{2+}/\text{Na}^+$ exchange reactions reported by Loizidou and Townsend (1987a) and Torres (1999) are listed in Table 4.

Loizidou and Townsend (1987b) also studied ion exchange between clinoptilolite (Na- and NH_4 -forms) and Pb^{2+} in solutions with nitrate as the co-anion. These

experiments showed that the $\text{Pb}^{2+}/\text{Na}^+$ exchange is reversible, whereas the $\text{Pb}^{2+}/\text{NH}_4^+$ exchange is irreversible. The irreversible behavior was argued to be due primarily to the ternary rather than binary nature of the exchange. For example, the NH_4 -form of clinoptilolite used in the experiments still had Na^+ in its structure, which apparently exchanged out when reacted with the $\text{Pb}^{2+}/\text{NH}_4^+$ solutions. Thermodynamic data for the $\text{Pb}^{2+}/\text{Na}^+$ exchange reaction reported by Loizidou and Townsend (1987b) are included in Table 4.

Pabalan (1994) and Pabalan and Bertetti (1999) conducted ion-exchange experiments involving homoionic Na- and K-clinoptilolite, prepared using zeolite material from Death Valley Junction, California, and aqueous mixtures of K^+/Na^+ , $\text{Ca}^{2+}/\text{Na}^+$, $\text{Sr}^{2+}/\text{Na}^+$, $\text{Sr}^{2+}/\text{K}^+$, and $\text{Ca}^{2+}/\text{K}^+$. The isotherm data were used to derive equilibrium constants and Gibbs free energies for the exchange reactions. The values, listed in Table 4, are significantly different from those derived by other investigators. The difference is mainly due to the different activity coefficient model used for the aqueous ions (Pabalan 1994). Pabalan and Bertetti (1999) checked the self-consistency of the Gibbs free energies for binary ion exchange using the triangle rule (Eqn. 19) on exchanges involving: (1) K^+/Na^+ , $\text{Ca}^{2+}/\text{Na}^+$, and $\text{Ca}^{2+}/\text{K}^+$; and (2) K^+/Na^+ , $\text{Sr}^{2+}/\text{Na}^+$, and $\text{Sr}^{2+}/\text{K}^+$. The value of $\Delta G_{(\text{Ca},\text{K})}^\circ$ calculated from $\Delta G_{(\text{Ca},\text{Na})}^\circ$ minus $2\Delta G_{(\text{K},\text{Na})}^\circ$ equals 20.1 ± 0.2 kJ/mol, which compares relatively well with the value 21.1 ± 0.5 kJ/mol derived from the $\text{K}^+/\text{Ca}^{2+}$ experiment. The value of $\Delta G_{(\text{Sr},\text{K})}^\circ$ calculated from $\Delta G_{(\text{Sr},\text{Na})}^\circ$ minus $2\Delta G_{(\text{K},\text{Na})}^\circ$ equals 18.8 ± 0.2 kJ/mol, significantly higher than the value 16.2 ± 0.3 J/mol derived from the $\text{K}^+/\text{Sr}^{2+}$ experiment. The authors argued that because experiments on $\text{K}^+/\text{Ca}^{2+}$ and $\text{K}^+/\text{Sr}^{2+}$ ion exchange, conducted at 0.05 N only, are more limited compared with the Na^+/K^+ , $\text{Na}^+/\text{Ca}^{2+}$, and $\text{Na}^+/\text{Sr}^{2+}$ experiments that were conducted at 0.005, 0.05, and 0.5 N, the derived $\Delta G_{(\text{Ca},\text{K})}^\circ$ and $\Delta G_{(\text{Sr},\text{K})}^\circ$ are not as well-constrained as $\Delta G_{(\text{K},\text{Na})}^\circ$, $\Delta G_{(\text{Ca},\text{Na})}^\circ$, and $\Delta G_{(\text{Sr},\text{Na})}^\circ$. The authors suggested that $\text{K}^+/\text{Ca}^{2+}$ and $\text{K}^+/\text{Sr}^{2+}$ experiments at other solution concentrations are needed to better constrain the regression of Equation (25) and the subsequent calculation of $\Delta G_{(\text{Sr},\text{K})}^\circ$ and $\Delta G_{(\text{Ca},\text{K})}^\circ$. The isotherm data of Pabalan (1994) and Pabalan and Bertetti (1999) were also used to derive parameters for the Margules solid-solution model, predict ion-exchange equilibria as a function of total solution concentration, and calculate aqueous compositions based on zeolite analysis. These calculations and the isotherm data from the two studies are presented in a later section.

Several other references have useful information on the ion-exchange properties of clinoptilolite. These references include White (1988), Dyer and Jozefowicz (1992), Chmielewska-Horvathova and Lesny (1992), Malliou et al. (1994), Pode et al. (1995), Tsukanova et al. (1995), Tarasevich et al. (1996), de Barros et al. (1997), Vucinic (1998b), Cooney et al. (1999), Loizidou et al. (1992), Ali et al. (1999), and Faghihian et al. (1999).

Erionite [$\text{NaK}_2\text{MgCa}_{1.5}(\text{Al}_8\text{Si}_{28}\text{O}_{72}) \cdot 28\text{H}_2\text{O}$]

The ion-exchange properties of erionite were studied by Sherry (1979). Natural erionite from Jersey Valley, Nevada, was converted to the Na-form by reacting with 1.0 N NaCl solutions at 298 K and 363 K. It was determined that two K^+ ions per unit cell, probably located in the cancrinite cages of the zeolite structure, could not be exchanged even after exhaustively exchanging with NaCl solutions, most likely due to steric hindrance. Isotherms for ion exchange with Li^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Sr^{2+} , and Ba^{2+} were determined at a total solution concentration of 0.1 N and at temperatures of 278 K and 298 K. Complete replacement of Na^+ by K^+ , Rb^+ , and Cs^+ was observed, but only incomplete exchange of Na^+ by Ca^{2+} , Sr^{2+} , and Ba^{2+} was attained. Sherry (1979) concluded that it is extremely difficult to replace all the exchangeable cations (those in large erionite cages) in natural erionite with divalent cations. The isotherm shapes of the

K^+/Na^+ , Rb^+/Na^+ , and Cs^+/Na^+ exchange reveal the strong preference of erionite for K^+ , Rb^+ , and Cs^+ ions over Na^+ . Isotherms for Ca^{2+}/Na^+ , Sr^{2+}/Na^+ , and Ba^{2+}/Na^+ show that erionite prefers Ca^{2+} , Sr^{2+} , and Ba^{2+} ions over Na^+ at low loading levels (i.e. at low values of \bar{E}_A), but this preference for the divalent cations drastically decreases with increasing loading, even reversing at high loadings. The selectivity series exhibited by erionite at low loadings is $Rb^+ > Cs^+ \geq K^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Na^+ > Li^+$. Equilibrium constants and Gibbs free energies were not calculated by Sherry (1979) from the isotherm data.

Chelishchev and Volodin (1977) conducted isotherm experiments on K^+/Na^+ , Cs^+/Na^+ , Li^+/Na^+ , and Rb^+/Cs^+ exchange using natural erionite from Georgia (of the former U.S.S.R.) at 293 K and total solution concentration of 0.1 N. The isotherm shapes are similar to those observed by Sherry (1979). However, in contrast to the results of Sherry (1979), Chelishchev and Volodin's data indicate that erionite has higher selectivity for Cs^+ than for Rb^+ . The selectivity series for erionite determined by Chelishchev and Volodin (1977) is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. Equilibrium constants and Gibbs free energies reported by Chelishchev and Volodin (1977) are listed in Table 5.

Ames (1964a,b) also studied the ion-exchange properties of natural erionite using material from Pine Valley, Nevada, that is 90% or higher in purity and has a CEC of 2.2 meq/g. Isotherms for Na^+/K^+ , Cs^+/Na^+ , Ca^{2+}/Na^+ , Sr^{2+}/Na^+ , and Sr^{2+}/Ca^{2+} exchange were determined at 298 K and 1.0 N solution concentration. In contrast to the results of Sherry (1979), the results of Ames (1964b) indicate that full exchange between Na^+ and the divalent cations Sr^{2+} and Ca^{2+} was achieved. The equilibrium constants and Gibbs free energies reported by Ames (1964a) are given in Table 5.

Ferrierite [(Na,K)Mg₂Ca_{0.5}(Al₆Si₃₀O₇₂)·20H₂O]

Ahmad and Dyer (1984) conducted experiments to determine the ease of replacement of Na^+ , K^+ , and Mg^{2+} ions in ferrierite by counterions (Na^+ , K^+ , NH_4^+ , Ca^{2+} , and Mg^{2+}) and mixtures of counterions (Na^+/K^+ , Na^+/NH_4^+ , K^+/NH_4^+ , Ca^{2+}/Mg^{2+}). The experiments used natural ferrierite from Lovelock, Nevada, purified by several sedimentations in a water column and sieving through a 150-mesh sieve. The CEC of the natural ferrierite, determined from the amount of K^+ , Na^+ , Ca^{2+} , and Mg^{2+} leached by a 1 M ammonium acetate solution, was 0.81 meq/g, which is less than the value of 1.88 meq/g¹¹ calculated by Ahmad and Dyer (1984) from the unit-cell composition of the ferrierite. The authors noted that 0.24 Mg^{2+} ions per unit cell were not available for exchange, possibly due to the occurrence of some of the Mg^{2+} in small cavities of the ferrierite structure. The results indicate that ferrierite is selective for NH_4^+ and K^+ and, to lesser degrees, for Na^+ , Ca^{2+} , and Mg^{2+} , but the selectivity for specific cations is diminished by the presence of other cations. Ahmad and Dyer (1984) also prepared a K-form of ferrierite from the 'as received' natural material, and they reacted the K-ferrierite with aqueous solutions of NH_4^+ , Na^+ , Rb^+ , Ag^+ , Cs^+ , Tl^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} (with Cl^- or NO_3^- as the co-anion). The amount of K^+ released from K-ferrierite by successive treatments of the counterions decreased in the order $Rb^+ > NH_4^+ \approx Cs^+ > Tl^+ > Ag^+ > Ba^{2+} > Mg^{2+} \approx Na^+ > Sr^{2+} > Ca^{2+}$.

Ahmad and Dyer (1988) conducted a more detailed study on the ion-exchange properties of ferrierite from Lovelock, Nevada. Isotherms for ion exchange between K-ferrierite and Na^+ , Rb^+ , Cs^+ , Ag^+ , Tl^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} were determined at a total solution concentration of 0.1 N and at temperatures in the range 297 to 353 K.

¹¹The CEC value of 1.08 meq/g given in Ahmad and Dyer (1984) is incorrect (pers. comm., A. Dyer, August 9, 2000).

Table 5. Literature values of equilibrium constants and Gibbs free energies for ion-exchange reactions involving erionite.

Ion-Exchange Reaction	$\ln K_{(A,B)}$	$\Delta G_{(A,B)}^{\circ}$ (kJ/mol)	Reference	Remarks
$\text{Li}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{LiL}$	-2.34	5.70	Chelishchev and Volodin (1977)	T = 293 K; Georgia (of the former U.S.S.R.) erionite
$\text{Rb}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{RbL}$	3.04	-7.41	Chelishchev and Volodin (1977)	T = 293 K; Georgia (of the former U.S.S.R.) erionite
$\text{K}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{KL}$	2.04	-4.97	Chelishchev and Volodin (1977)	T = 293 K; Georgia (of the former U.S.S.R.) erionite
$\text{K}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{KL}$	2.40	-5.94	Ames (1964a)	T = 298 K; Pine Valley, Nevada erionite; CEC = 2.2 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	4.52	-11.0	Chelishchev and Volodin (1977)	T = 293 K; Georgia (of the former U.S.S.R.) erionite
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	3.49	-8.65	Ames (1964a)	T = 298 K; Pine Valley, Nevada erionite; CEC = 2.2 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	2.86	-8.16	Ames (1964a)	T = 343 K; Pine Valley, Nevada erionite; CEC = 2.2 meq/g
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	0.0488	-0.12	Ames (1964b)	T = 298 K; Pine Valley, Nevada erionite; CEC = 2.2 meq/g
$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-0.231	0.57	Ames (1964b)	T = 298 K; Pine Valley, Nevada erionite; CEC = 2.2 meq/g
$\text{Sr}^{2+} + \text{CaL}_2 \Leftrightarrow \text{Ca}^{2+} + \text{SrL}_2$	-0.277	0.69	Ames (1964b)	T = 298 K; Pine Valley, Nevada erionite; CEC = 2.2 meq/g

The results indicate that the ion-exchange reactions were reversible within the composition and temperature ranges examined except for Ag^+/K^+ exchange, which had unusual features at high values of \bar{E}_{Ag} . Rb^+ , Cs^+ , and Tl^+ were preferred by ferrierite over K^+ . In all cases except Ag^+ , an increase in temperature increased the extent of replacement of K^+ by the incoming cation, although the temperature effect for Tl^+ is very small. The isotherm data were extrapolated to obtain the maximum equivalent fraction of the ingoing cation in the zeolite. Equilibrium constants and Gibbs free energies were derived from the normalized isotherm data. The Gibbs free energies at 297 K reported by Ahmad and Dyer (1988) and the corresponding equilibrium constants are listed in Table 6. From the Gibbs free energies, the authors determined the following affinity sequence for ferrierite: $\text{Tl}^+ \approx \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ag}^+ > \text{Na}^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$.

Townsend and Loizidou (1984) also used ferrierite from Lovelock, Nevada, in their ion-exchange experiments involving $\text{Na}^+/\text{NH}_4^+$ mixtures. As in the studies by Ahmad and Dyer (1984, 1988), the natural material was purified by a sedimentation procedure to remove the fines. A homoionic Na-ferrierite was prepared by exchange with NaNO_3 solution at 298 K and also at 343 K. The isotherm for $\text{NH}_4^+/\text{Na}^+$ exchange was determined at 298 K and a total solution concentration of 0.1 N. Although the ferrierite had a CEC of 1.80 meq/g based on the Al^{3+} content of the zeolite, a maximum level of exchange, $\bar{E}_{\text{NH}_4^+/\text{Na}^+}$, of only 0.499 was achieved. The $\text{NH}_4^+/\text{Na}^+$ isotherm shape is similar to the $\text{NH}_4^+/\text{Na}^+$ results for mordenite. However, in contrast to the mordenite results, the solution analyses confirmed that the ion exchange with ferrierite was ternary in nature; K^+ , along with Na^+ , was released from the zeolite upon reaction with the $\text{NH}_4^+/\text{Na}^+$ solutions. Townsend and Loizidou (1984) noted that at low $\bar{E}_{\text{NH}_4^+/\text{Na}^+}$, NH_4^+ exchanged principally with Na^+ . It was only as $\bar{E}_{\text{NH}_4^+/\text{Na}^+}$ increased that significant quantities of K^+ were also involved in the exchange reaction. No thermodynamic parameters for this system were derived because of the ternary nature of the exchange reactions.

Loizidou and Townsend (1987a) reported isotherms for ion exchange between Na- and NH_4 -ferrierite, prepared from natural ferrierite from Lovelock, Nevada, and mixtures of $\text{Pb}^{2+}/\text{Na}^+$ and $\text{Pb}^{2+}/\text{NH}_4^+$ (0.1 or 0.5 N; NO_3^- co-anion). Maximum levels of exchange, $\bar{E}_{\text{Pb}^{2+}/\text{Na}^+}$, determined for systems with Na^+ and NH_4^+ as the counter-cations were 0.506 and 0.486, respectively. The $\text{Pb}^{2+}/\text{NH}_4^+$ solutions analyzed after exchange contained only Pb^{2+} and NH_4^+ ions plus a trace of Ca^{2+} , indicating that the reaction is essentially binary. On the other hand, the $\text{Pb}^{2+}/\text{Na}^+$ exchange was irreversible due to the ternary nature of the exchange reaction. K^+ ions in the zeolite, which had not been removed by exhaustive exchanges with NaNO_3 during the preparation of the 'homoionic' Na-ferrierite, were released into solution when the zeolite was reacted with $\text{Pb}^{2+}/\text{Na}^+$ mixtures. Thermodynamic values for $\text{Pb}^{2+}/\text{NH}_4^+$ exchange reported by Loizidou and Townsend (1987b) are listed in Table 6.

In a separate study, Loizidou and Townsend (1987b) also measured isotherms for $\text{Cd}^{2+}/\text{Na}^+$ and $\text{Cd}^{2+}/\text{NH}_4^+$ exchange at 298 K (0.1 N; Cl^- or NO_3^- co-anion). The results show that both exchange reactions are reversible. Only traces of Ca^{2+} and no K^+ were found in solution after $\text{Cd}^{2+}/\text{Na}^+$ exchange, and negligible quantities of Ca^{2+} and K^+ were found in solution after $\text{Cd}^{2+}/\text{NH}_4^+$ exchange. Maximum levels of exchange, $\bar{E}_{\text{Cd}^{2+}/\text{Na}^+}$, determined for the $\text{Cd}^{2+}/\text{Na}^+$ and $\text{Cd}^{2+}/\text{NH}_4^+$ systems are 0.339 and 0.280, respectively, independent of the co-anion. Similar to the other zeolites, ferrierite shows stronger selectivity for Cd^{2+} when NO_3^- is the co-anion rather than Cl^- due to the complexation of Cd^{2+} with Cl^- . In addition, the Na-ferrierite shows a higher preference for Cd^{2+} than the NH_4 -ferrierite. Thermodynamic parameters reported by Loizidou and Townsend (1987b), listed in Table 6, indicate that Cd^{2+} is not preferred over Na^+ or NH_4^+ by ferrierite.

Table 6. Literature values of equilibrium constants and Gibbs free energies for ion-exchange reactions involving ferrierite.

Ion-Exchange Reaction	$\ln K_{(A,B)}$	$\Delta G_{(A,B)}^{\circ}$ (kJ/mol)*	Reference	Remarks
$\text{Na}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{NaL}$	-0.089	0.22	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Rb}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{RbL}$	1.38	-3.42	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Cs}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{CsL}$	1.98	-4.90	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{NH}_4^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{NH}_4\text{L}$	0.948	-2.34	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Ag}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{AgL}$	0.33	-0.82	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{TI}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{TIL}$	1.99	-4.91	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Mg}^{2+} + 2\text{KL} \Leftrightarrow 2\text{K}^+ + \text{MgL}_2$	-3.82	9.44	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Ca}^{2+} + 2\text{KL} \Leftrightarrow 2\text{K}^+ + \text{CaL}_2$	-3.63	8.96	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Sr}^{2+} + 2\text{KL} \Leftrightarrow 2\text{K}^+ + \text{SrL}_2$	-2.79	6.88	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Ba}^{2+} + 2\text{KL} \Leftrightarrow 2\text{K}^+ + \text{BaL}_2$	-2.02	4.98	Ahmad and Dyer (1988)	T = 297 K; Lovelock, Nevada ferrierite; normalized isotherm
$\text{Pb}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{PbL}_2$	-1.15	2.84	Loizidou and Townsend (1987a)	T = 298K; Lovelock, Nevada ferrierite; isotherm data normalized to $\bar{E}_{\text{Pb,max}}$ of 0.486
$\text{Cd}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CdL}_2$	-1.36 (Cl ⁻ co-anion)	3.36 (Cl ⁻ co-anion)	Loizidou and Townsend (1987b)	T = 298K; Lovelock, Nevada ferrierite; isotherm data normalized to $\bar{E}_{\text{Cd,max}}$ of 0.339
	-1.65 (NO ₃ ⁻ co-anion)	4.10 (NO ₃ ⁻ co-anion)		
$\text{Cd}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{CdL}_2$	-2.95 (Cl ⁻ co-anion)	7.32 (Cl ⁻ co-anion)	Loizidou and Townsend (1987b)	T = 298K; Lovelock, Nevada ferrierite; isotherm data normalized to $\bar{E}_{\text{Cd,max}}$ of 0.280
	-2.40 (NO ₃ ⁻ co-anion)	5.96 (NO ₃ ⁻ co-anion)		

*Values from Ahmad and Dyer (1988) and Loizidou and Townsend (1987a,b), given in kilojoules per equivalent, were converted to kilojoules per mole.

Heulandite [(Na,K)Ca₄(Al₉Si₂₇O₇₂)·24H₂O]

Ames (1968) conducted K⁺/Na⁺, Cs⁺/K⁺, and Cs⁺/Na⁺ ion-exchange experiments using samples of heulandite (>95% pure) from Bay of Fundy, Nova Scotia. The material, with grain size in the range 0.25 to 0.50 mm, had a CEC of 0.43 meq/g, much lower than the CECs measured by Ames (1964a,b; 1968) for Hector and Pierre clinoptilolite (1.70 and 1.32 meq/g, respectively). The lower CEC of the 0.25 to 0.50 mm heulandite was explained as probably due to crystal 'stacking faults,' which presumably reduced the accessible intracrystalline exchange sites in the heulandite sample. The CEC of the heulandite increased to 1.02 meq/g when ground to <200 mesh (Ames 1968). The isotherm points for the K⁺/Na⁺ couple lie along a trend coincident with the K⁺/Na⁺ isotherm for clinoptilolite reported in the same study. The Cs⁺/Na⁺ isotherm indicates that heulandite prefers Cs⁺ over Na⁺, similar to clinoptilolite, although heulandite is less selective for Cs⁺ compared with clinoptilolite. On the other hand, the data for Cs⁺/K⁺ exchange show that heulandite is selective for K⁺ relative to Cs⁺, in contrast to the preference of clinoptilolite for Cs⁺ relative to K⁺. The sigmoidal-shaped isotherms presented by Ames (1968) for both Cs⁺/K⁺ and Cs⁺/Na⁺ exchange suggest that selectivity reversal occurs at an intermediate heulandite composition. Thermodynamic parameters reported by Ames (1968) are listed in Table 7.

Table 7. Equilibrium constants and Gibbs free energies for ion exchange at 296 K involving a heulandite specimen from Bay of Fundy, Nova Scotia (CEC = 0.43 meq/g). Data from Ames (1968).

Ion-Exchange Reaction	ln K _(A,B)	ΔG [°] _(A,B) (kJ/mol)
K ⁺ + NaL ⇌ Na ⁺ + KL	2.43	-5.98
Cs ⁺ + NaL ⇌ Na ⁺ + CsL	1.36	-3.35
Cs ⁺ + KL ⇌ K ⁺ + CsL	-0.75	1.85

Ion-exchange studies using Siberian heulandite and Bulgarian clinoptilolite were conducted by Filizova (1974). The author determined the selectivity series K > Rb > Na > Li > Sr > Ba > Ca for heulandite, and the sequence Rb > K > Na > Ba > Sr > Ca > Li for clinoptilolite.

Al'tshuler and Shkurenko (1990, 1997) presented experimental data on ion exchange involving heulandite (CEC = 2.20 meq/g) and Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, NH₄⁺, Ca²⁺, and Pb²⁺ from which they determined the selectivity series Cs⁺ > Rb⁺ > Pb²⁺, K⁺ > NH₄⁺ > Ca²⁺ > Na⁺ > Li⁺, which is somewhat inconsistent with the selectivity series determined by Filizova (1974). Al'tshuler and Shkurenko (1992) also conducted microcalorimetric measurements at 303 K of the heat effects of heulandite ion exchange. Their results show that the enthalpies of ion exchange decrease in the order Na⁺ > NH₄⁺ > K⁺ > Rb⁺ > Cs⁺. In addition, Al'tshuler et al. (1996) reacted heulandite with binary mixtures of NaCl, NiCl₂, CuCl₂, ZnCl₂, and MnCl₂, and determined the selectivity series Mn²⁺ > Na⁺ > Zn²⁺ > Cu²⁺ > Ni²⁺.

Laumontite [Ca₄(Al₈Si₁₆O₄₈)·16H₂O]

A natural laumontite from Bernisdale, Isle of Skye, Scotland, was examined by Dyer et al. (1991) as a candidate material for treating aqueous nuclear wastes. The material was ground and sieved to a 150–240 mesh fraction and was converted to a maximum Ca-

exchanged form by repeated contact with 1 M CaCl₂ solution. The CEC of the zeolite, measured at different pHs, is 2.38, 3.73, 3.94, and 6.18 meq/g at a pH of 5, 8, 9.5, and 11.4, respectively. Isotherms for NH₄⁺/Ca²⁺, K⁺/Ca²⁺, Cs⁺/Ca²⁺, and Sr²⁺/Ca²⁺ exchange were determined at room temperature and a total solution concentration of 0.01 N. The results show that laumontite prefers Ca²⁺ over K⁺, NH₄⁺, Na⁺, and Cs⁺, but the zeolite is selective for Sr²⁺ relative to Ca²⁺. The isotherms for Na⁺/Ca²⁺, Cs⁺/Ca²⁺, NH₄⁺/Ca²⁺, K⁺/Ca²⁺ exchange are very similar.

Mordenite [Na₃KCa₂(Al₈Si₄₀O₉₆)·28H₂O]

Both natural and synthetic forms of mordenite have been studied extensively, and the use of synthetic mordenites in industry is common. However, there are distinct differences in the ion-exchange behavior of natural and synthetic mordenites. Because of these differences, several studies of synthetic mordenite are also discussed in this section.

Ames (1961) used a column apparatus to load natural zeolite samples with Cs⁺ and competing cations to determine the selectivity of the zeolites and to gain insight into the mechanisms responsible for a particular selectivity sequence. Natural mordenite crystals from Nova Scotia, Canada, hand-picked to greater than 95% purity, were exposed to solutions of alkali and alkaline-earth cations at a total concentration of 0.01 N and a temperature of 298 K. Ames' results indicated a selectivity sequence of Cs⁺ > K⁺ > Na⁺ > Li⁺ for alkali metals and Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺ for alkaline earths.

In more extensive studies of the ion exchange of alkali metal cations and alkaline-earth cations in zeolites, Ames (1964a,b) conducted experiments on two types of mordenite: (1) AW-300, commercially available in the Na-form but prepared from natural mordenite, and (2) Zeolon, a synthetic mordenite also commercially available in the Na-form. The CECs of the commercial mordenites were determined to be 1.6 and 1.9 meq/g for the AW-300 and Zeolon, respectively. Ion-exchange experiments were conducted at 298 and 343 K with a solution total normality of 1.0 N. Isotherms are presented in Ames (1964a) for Na⁺/Cs⁺, K⁺/Cs⁺, K⁺/Na⁺ for AW-300 and K⁺/Na⁺ for Zeolon. The isotherms for Na⁺/Cs⁺ and K⁺/Cs⁺ exchange on AW-300 presented by Ames (1964a) suggest that incomplete exchange occurred. In contrast, the synthetic Zeolon mordenite exhibited complete exchange. The difference in the exchange behavior of AW-300 and Zeolon was explained by Ames (1964a) as due to the presence of 'stacking faults,' present in AW-300 but not in Zeolon. Thermodynamic data generated by Ames (1964a,b) for AW-300 and Zeolon are listed in Table 8.

Lu et al. (1981) produced ion-exchange isotherms for NH₄⁺/Ag⁺ and NH₄⁺/K⁺ systems using natural and synthetic mordenite. Experiments were conducted at 0.22 N total solution concentration and 298 K using a near homoionic NH₄-form of mordenite. Calculated CECs for the natural and synthetic mordenite were 2.17 and 2.19 meq/g, respectively. Differences in calculated ion-exchange equilibrium constants and Gibbs free energies between the natural and synthetic mordenite were attributed to 'stacking faults' within the natural mordenite. Thermodynamic values derived from the Lu et al. (1981) experiments are listed in Table 8.

Townsend and Loizidou (1984) investigated Na⁺/NH₄⁺ exchange equilibria for natural mordenite from Lovelock, Nevada. Ion-exchange experiments were conducted at 298 K and a solution concentration of 0.1 N (NO₃⁻ co-anion). A near homoionic Na-form of mordenite, with a calculated CEC of 2.11 meq/g based on the Al³⁺ content, was exchanged with NH₄⁺. The results indicated that the exchange was reversible but incomplete, with only a 50.1% maximal level of exchange achieved. This result was in marked contrast to results for synthetic mordenite, which showed exchange to 100% of

the calculated CEC (Barrer and Klinowski 1974b). The authors suggested that the differences in exchange properties between natural and synthetic mordenite may be due to 'stacking faults' within the natural mordenite crystal structure as originally proposed by Ames (1964a) and by Lu et al. (1981). Thermodynamic values derived by Townsend and Loizidou (1984) are listed in Table 8.

In follow-up studies of ion exchange in natural zeolites, Loizidou and Townsend (1987a,b) investigated the exchange of Pb^{2+} and Cd^{2+} on Na- and NH_4 -forms of natural mordenite from Lovelock, Nevada. In one study (Loizidou and Townsend 1987b), near homoionic Na- and NH_4 -forms of mordenite were exchanged with Pb^{2+} -bearing solutions at two different concentrations, 0.1 and 0.5 N (NO_3^- co-anion). Incomplete exchange was observed for both Na- and NH_4 -forms of the zeolite. The Na-form exhibited a higher selectivity for Pb^{2+} than the NH_4 -form. As with $\text{Na}^+/\text{NH}_4^+$ exchange studied previously (Townsend and Loizidou 1984), $\text{Pb}^{2+}/\text{Na}^+$ and $\text{Pb}^{2+}/\text{NH}_4^+$ exchanges were reversible, but values of $\bar{E}_{\text{Pb,max}}$ for the Na^+ and NH_4^+ counter-ions were found to be 0.490 and 0.517, respectively, values that are probably equal within experimental uncertainty. Likewise, values of $\bar{E}_{\text{Pb,max}}$ were independent of the total normality of the solutions. At similar solution concentrations, the Na-mordenite was more selective for Pb^{2+} than the NH_4^+ -form.

In contrast to the Pb^{2+} study, Loizidou and Townsend (1987a) observed that Cd^{2+} was preferred by neither the Na- nor the NH_4 -form of natural mordenite. In their study, Cd^{2+} -bearing solutions at a total concentration of 0.1 N and a temperature of 298 K were exchanged with Na- and NH_4 -forms of natural mordenite. The effect of using Cl^- or NO_3^- as the co-anion was also investigated. Although the exchanges were reversible, incomplete exchange was again observed, with the values for $\bar{E}_{\text{Cd,max}}$ reaching only 0.334 and 0.327 for the Na- and NH_4 -forms, respectively. Interestingly, although the choice of co-anion affected the resulting thermodynamic values calculated for the exchange of Cd^{2+} (mordenite was less selective for Cd^{2+} when Cl^- was the co-anion), it did not affect the value of $\bar{E}_{\text{Cd,max}}$. Differences in selectivity due to co-anion type were attributed to differences in aqueous complexation of Cd^{2+} . Thermodynamic values from Loizidou and Townsend (1987a,b) are listed in Table 8.

Liang and Hsu (1993) studied the sorption of Cs^+ and Sr^{2+} on natural mordenite and interpreted the results using a Freundlich isotherm model. Temperature (298 and 363 K) and pH (2) effects were investigated. The results indicated that temperature did not have a significant effect for Cs^+ exchange, but an increase in temperature did enhance the sorption of Sr^{2+} . Sorption of both Cs^+ and Sr^{2+} was reduced at low pH, probably due to ion-exchange competition from H^+ . Cs^+ was preferentially exchanged over Sr^{2+} .

Barrer and Klinowski (1974b) measured isotherms for a synthetic mordenite (Zeolon), which was prepared in Na- and NH_4 -forms for their experiments. Experiments were conducted for the Na^+/Cs^+ , NH_4^+/K^+ , $\text{NH}_4^+/\text{Na}^+$, $\text{NH}_4^+/\text{Li}^+$, $\text{NH}_4^+/\text{Ca}^{2+}$, $\text{NH}_4^+/\text{Sr}^{2+}$, and $\text{NH}_4^+/\text{Ba}^{2+}$ systems at 298 K using a total solution concentration of 0.05 N. All reactions were reversible except those involving Ca^{2+} and Sr^{2+} . A thermodynamic affinity sequence of $\text{Cs}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ba}^{2+} > \text{Li}^+$ was established. The selectivity sequence for alkali metals was similar to other zeolites, provided that normalization was used to compensate for incomplete exchange. Comparison of Na^+/Cs^+ exchange between natural and synthetic mordenite showed that the selectivity for Cs^+ relative to Na^+ was greater in the synthetic sample.

Barrer and Townsend (1976a) conducted an ion-exchange study of Zeolon (NH_4 -form) and several transition metals. Experiments were conducted at 298 K and a solution total normality of 0.08 N. None of the metals exchanged completely, with maximum

Table 8. Literature values of equilibrium constants and Gibbs free energies for ion-exchange reactions involving mordenite.

Ion-Exchange Reaction	$\ln K_{(A,B)}$	$\Delta G_{(A,B)}^\circ$ (kJ/mol)*	Reference	Remarks
$H^+ + NaL \rightleftharpoons Na^+ + HL$	1.67	-3.86	Wolf et al. (1978)	T = 278 K; synthetic
	1.67	-4.07		T = 293 K; synthetic
$H^+ + KL \rightleftharpoons H^+ + KL$	-1.19	2.76	Wolf et al. (1978)	T = 274 K; synthetic
	-1.36	3.31		T = 293 K; synthetic
$Li^+ + HL \rightleftharpoons H^+ + LiL$	-5.3	13.0	Golden & Jenkins (1981)	T = 298 K; H-Zeolon
$Li^+ + NaL \rightleftharpoons Na^+ + LiL$	-3.0	7.5	Golden & Jenkins (1981)	T = 298 K; Na-Zeolon
$Na^+ + KL \rightleftharpoons K^+ + NaL$	-1.94	4.82	Ames (1964a)	T = 298 K; Zeolon
$Na^+ + KL \rightleftharpoons K^+ + NaL$	-3.0	7.4	Ames (1964a)	T = 298 K; AW-300
$K^+ + NaL \rightleftharpoons Na^+ + KL$	2.45	-5.58	Wolf et al. (1978)	T = 278 K; synthetic
	2.22	-5.42		T = 293 K; synthetic
$K^+ + NH_4L \rightleftharpoons NH_4^+ + KL$	0.456	-1.129	Lu et al. (1981)	T = 298 K; synthetic
$K^+ + NH_4L \rightleftharpoons NH_4^+ + KL$	0.539	-1.335	Lu et al. (1981)	T = 298 K; natural
$Cs^+ + NaL \rightleftharpoons Na^+ + CsL$	3.37	-8.36	Ames (1964a)	T = 298 K; Zeolon
$Cs^+ + NaL \rightleftharpoons Na^+ + CsL$	0.596	-1.475	Ames (1964a)	T = 298 K; AW-300
				equilibrium may not have been attained
$Cs^+ + NaL \rightleftharpoons Na^+ + CsL$	3.30	-8.18	Barrer & Klinowski (1974b)	T = 298 K; Zeolon
$Cs^+ + NaL \rightleftharpoons Na^+ + CsL$	2.91	-8.29	Ames (1964a)	T = 343 K; Zeolon
$Cs^+ + NaL \rightleftharpoons Na^+ + CsL$	1.02	-2.92	Ames (1964a)	T = 343 K; AW-300
$Cs^+ + KL \rightleftharpoons K^+ + CsL$	-0.569	1.41	Ames (1964a)	T = 298 K; AW-300; equilibrium may not have been attained
$Cs^+ + KL \rightleftharpoons K^+ + CsL$	1.52	-3.76	Ames (1964a)	T = 298 K; Zeolon
$Cs^+ + KL \rightleftharpoons K^+ + CsL$	1.41	-4.02	Ames (1964a)	T = 343 K; Zeolon
$NH_4^+ + LiL \rightleftharpoons Li^+ + NH_4^+L$	4.44	-11.0	Barrer & Klinowski (1974b)	T = 298 K; Zeolon
$NH_4^+ + NaL \rightleftharpoons Na^+ + NH_4L$	1.52	-3.76	Barrer & Klinowski (1974b)	T = 298 K; Zeolon
$NH_4^+ + NaL \rightleftharpoons Na^+ + NH_4L$	1.86	-4.590	Townsend & Loizidou (1984)	T = 298 K; NO_3^- co-anion; Lovelock, Nevada mordenite; normalized isotherm

$\text{NH}_4^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{NH}_4^+\text{L}$	-0.467	1.16	Barrer & Klinowski (1974b)	T = 298 K; Zeolon
$\text{Ag}^+ + \text{NH}_4\text{L} \Leftrightarrow \text{NH}_4^+ + \text{AgL}$	0.785	-1.946	Lu et al. (1981)	T = 298 K; synthetic
$\text{Ag}^+ + \text{NH}_4\text{L} \Leftrightarrow \text{NH}_4^+ + \text{AgL}$	0.724	-1.793	Lu et al. (1981)	T = 298 K; natural
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	-0.370	0.916	Ames (1964b)	T = 298 K; Zeolon
$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-1.45	3.59	Ames (1964b)	T = 298 K; Zeolon
$\text{Sr}^{2+} + \text{CaL} \Leftrightarrow \text{Ca}^{2+} + \text{SrL}_2$	-1.15	2.85	Ames (1964b)	T = 298 K; Zeolon
$\text{Ba}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{BaL}_2$	-4.14	10.2	Barrer & Klinowski (1974b)	T = 298 K; Zeolon
$\text{Cd}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{CdL}_2$	-2.3 (Cl ⁻)	5.78 (Cl ⁻)	Loizidou & Townsend (1987a)	T = 298 K; Lovelock, Nevada mordenite; normalized isotherm
$\text{Cd}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CdL}_2$	-0.99 (NO ₃ ⁻)	2.46 (NO ₃ ⁻)	Loizidou & Townsend (1987a)	T = 298 K; Lovelock, Nevada mordenite; normalized isotherm
$\text{Co}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CoL}_2$	-0.896 (Cl ⁻)	2.22 (Cl ⁻)	Golden & Jenkins (1981)	T = 298 K; Na-Zeolon
$\text{Co}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{CoL}_2$	-0.870 (NO ₃ ⁻)	2.16 (NO ₃ ⁻)	Barrer & Townsend (1976b)	T = 298 K; NH ₄ -Zeolon, normalized isotherm
$\text{Cu}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{CuL}_2$	-0.46	1.1	Barrer & Townsend (1976b)	T = 298 K; NH ₄ -Zeolon, normalized isotherm
$\text{Mn}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{MnL}_2$	-3.57	8.84	Barrer & Townsend (1976b)	T = 298 K; NH ₄ -Zeolon, normalized isotherm
$\text{Ni}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{NiL}_2$	-3.24	8.04	Barrer & Townsend (1976b)	T = 298 K; NH ₄ -Zeolon, normalized isotherm
$\text{Pb}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{PbL}_2$	-3.11	7.72	Barrer & Townsend (1976b)	T = 298 K; NH ₄ -Zeolon, normalized isotherm
$\text{Pb}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{PbL}_2$	-3.64	9.02	Barrer & Townsend (1976b)	T = 298 K; NH ₄ -Zeolon, normalized isotherm
$\text{Zn}^{2+} + 2\text{NH}_4\text{L} \Leftrightarrow 2\text{NH}_4^+ + \text{ZnL}_2$	3.750 (at 0.1N) 2.841 (at 0.5N)	-9.29 (at 0.1N) -7.04 (at 0.5N)	Loizidou & Townsend (1987b)	T = 298 K; NO ₃ ⁻ co-anion; Lovelock, Nevada mordenite; normalized isotherm
	-2.66	6.59	Loizidou & Townsend (1987b)	T = 298 K; NO ₃ ⁻ co-anion; Lovelock, Nevada mordenite; normalized isotherm
	-3.60	8.92	Barrer & Townsend (1976b)	T = 298 K; NH ₄ -Zeolon, normalized isotherm

*Values from Loizidou and Townsend (1987a,b), Barrer and Klinowski (1974b), and Barrer and Townsend (1976b), given in kilojoules per equivalent, were converted to kilojoules per mole.

levels of exchange less than 50%. The isotherm results were normalized for thermodynamic analysis using values of $\bar{E}_{\text{Co,max}}$, $\bar{E}_{\text{Mn,max}}$, $\bar{E}_{\text{Zn,max}}$, $\bar{E}_{\text{Ni,max}}$, and $\bar{E}_{\text{Cu,max}}$ equal to 0.467, 0.470, 0.470, 0.416, and 0.483, respectively. Varying the pH (from 4 to 7) and the co-anion (acetate, formate, and chloride) did not appear to affect exchange significantly. A thermodynamic affinity sequence was established as $\text{Cs}^+ > \text{NH}_4^+ \approx \text{K}^+ > \text{Ba}^+ > \text{Sr}^{2+} \approx \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} \approx \text{Zn}^{2+} > \text{Ni}^{2+}$ for NH_4 -mordenite. Barrer and Townsend (1976a) made full use of the triangle rule to estimate ion-exchange affinities of synthetic mordenite and to compare exchange between Na- and NH_4 -mordenite. Thermodynamic values derived by Barrer and Townsend (1976a) from the experimental data are given in Table 8.

Suzuki et al. (1978) determined cation-exchange isotherms for several alkali metal and alkaline-earth cations, H^+ , and NH_4^+ . The experiments used a Na-form of synthetic mordenite and were conducted at 298 K using solutions with a total normality of 0.1 N. The authors determined that synthetic mordenite preferred monovalent cations relative to divalent cations. A general selectivity sequence of $\text{Cs}^+ > \text{NH}_4^+ \approx \text{K}^+ \approx \text{H}^+ > \text{Ba}^+ > \text{Sr}^{2+} \approx \text{Ca}^{2+} > \text{Rb}^+ > \text{Mg}^{2+}$ was postulated. The shape of the isotherms presented suggests that ion exchange was incomplete for several cations.

Isotherms of K^+/Na^+ , H^+/Na^+ , and H^+/K^+ exchange on a Na-form of synthetic mordenite are presented in Wolf et al. (1978). Experiments were conducted at 274, 278, and 293 K using a total solution concentration of 0.6 N, and they illustrate the temperature effects on ion exchange in synthetic mordenite. The CEC for the mordenite was determined to be 2.13 meq/g. Thermodynamic values determined by Wolf et al. (1978) are provided in Table 8.

Golden and Jenkins (1981) generated isotherms for synthetic mordenite (Zeolon) for Na^+/Li^+ , $\text{Na}^+/\text{Co}^{2+}$, and H^+/Li^+ exchange. The experiments were conducted at 298 K with a total solution concentration of 0.1 N. Reversibility was demonstrated in all three systems, although the exchange of Co^{2+} was incomplete. The results of thermodynamic calculations generally agreed with results from other investigations (e.g. Barrer and Klinowski 1974b), and the triangle rule was successfully applied for Na^+/Li^+ and $\text{Na}^+/\text{Co}^{2+}$. The thermodynamic data of Golden and Jenkins (1981) are listed in Table 8.

Kuznetsova et al. (1998) recently described the ion-exchange properties of synthetic mordenite based on a strong electrolyte model. Reasonable agreement with the equilibrium constants derived by Barrer and Klinowski (1974b) was achieved.

Other papers regarding ion exchange on mordenite that may be of interest include Gradev and Gulubova (1982), an investigation of the uptake of ^{134}Cs , ^{137}Cs , ^{89}Sr , and ^{90}Sr on natural clinoptilolite and mordenite, and Grebenshchikova et al. (1973a,b), who investigated the uptake of Pu^{4+} and Th^{4+} on a Na-form of mordenite at low pH.

Phillipsite [$\text{K}_2(\text{Ca}_{0.5}\text{Na})_4(\text{Al}_6\text{Si}_{10}\text{O}_{32}) \cdot 12\text{H}_2\text{O}$]

Ion exchange of Cs^+ and Sr^{2+} for Na^+ in three types of phillipsite—sedimentary, hydrothermal, and synthetic—was studied by Adabbo et al. (1999) at 298 K and 0.1 N solution concentration. The sedimentary phillipsite material was prepared from a phillipsite-rich rock from Marano, Italy, whereas the hydrothermal phillipsite was obtained from cavities and vugs of a basalt sample from Vesuvius, Italy. The synthetic phillipsite was prepared hydrothermally from oxide mixtures. The measured CECs are 3.55, 4.71, and 3.60 meq/g for the sedimentary, hydrothermal, and synthetic phillipsite, respectively. For comparison, the CECs calculated from the aluminum content of the zeolites are 3.66, 4.70, and 3.52 meq/g, for the sedimentary, hydrothermal, and synthetic phillipsite, respectively. The results indicate that the Cs^+/Na^+ and $\text{Sr}^{2+}/\text{Na}^+$ exchange reactions are reversible for the three types of phillipsite and the total CEC of the three

zeolites is available for Cs^+ and Sr^{2+} exchange. The sedimentary and synthetic phillipsites, characterized by a higher Si/Al ratio than the hydrothermal zeolite, display good selectivity for Cs^+ and moderate selectivity for Sr^{2+} , whereas the more aluminous hydrothermal phillipsite has lower selectivity for Cs^+ and higher selectivity for Sr^{2+} compared with the sedimentary and synthetic phillipsites. The Cs^+/Na^+ isotherm for hydrothermal phillipsite exhibits a selectivity reversal, not observed for the sedimentary and synthetic phillipsites, at an $\bar{E}_{\text{Cs,max}}$ of about 0.73. The $\text{Sr}^{2+}/\text{Na}^+$ isotherms for the sedimentary, synthetic, and hydrothermal zeolite exhibit selectivity reversal at $\bar{E}_{\text{Cs,max}}$ equal to 0.15, 0.18, and 0.69, respectively. The equilibrium constants and Gibbs free energies reported by Adabbo et al. (1999) are listed in Table 9.

Isotherm data on ion exchange between phillipsite and $\text{Pb}^{2+}/\text{Na}^+$ and $\text{Pb}^{2+}/\text{K}^+$ solutions (NO_3^- co-anion) at 0.1 N total solution concentration were reported by Pansini et al. (1996). The Na- and K-phillipsite were obtained by purifying phillipsite-rich tuff from Chiaiano, Naples, Italy, and exchanging with 0.5 M NaCl or KCl solutions. The measured CEC of the phillipsite material is 3.30 meq/g. The results show that Pb^{2+} exchange for Na^+ and K^+ is reversible. Phillipsite exhibits a strong affinity for Pb^{2+} relative to Na^+ , with the $\text{Pb}^{2+}/\text{Na}^+$ isotherm lying above the diagonal over the whole composition range. The $\text{Pb}^{2+}/\text{K}^+$ isotherm shows a selectivity reversal at an \bar{E}_{pb} of about 0.37. Below this value, phillipsite exhibits a moderate selectivity for Pb^{2+} . Thermodynamic parameters reported by Pansini et al. (1996) are listed in Table 9.

Colella et al. (1998) used Na-phillipsite obtained by purifying phillipsite-rich tuff from Marano, Italy, and exhaustively exchanging with NaCl solutions. The measured CEC of the zeolite is 3.30 meq/g. Isotherms for $\text{Cu}^{2+}/\text{Na}^+$ and $\text{Zn}^{2+}/\text{Na}^+$ exchange were determined at 298 K and 0.1 N solution concentration (NO_3^- co-anion). The results indicate that the $\text{Zn}^{2+}/\text{Na}^+$ exchange is reversible, but the $\text{Cu}^{2+}/\text{Na}^+$ exchange is irreversible—the isotherm shows an obvious hysteresis loop. Incomplete exchange was observed for both $\text{Cu}^{2+}/\text{Na}^+$ and $\text{Zn}^{2+}/\text{Na}^+$ reactions, with $\bar{E}_{\text{Cu,max}}$ and $\bar{E}_{\text{Zn,max}}$ equal to 0.76 and 0.73, respectively. The isotherms show that phillipsite has poor selectivity for both Cu^{2+} and Zn^{2+} . The thermodynamic parameters for $\text{Zn}^{2+}/\text{Na}^+$ exchange reported by Colella et al. (1998) are listed in Table 9.

Chelishchev et al. (1984) reported isotherm data on K^+/Na^+ , Rb^+/Na^+ , Cs^+/Na^+ , and Li^+/Na^+ exchange based on experiments at 295 K and 1 N solution concentration using phillipsite material from Georgia (of the former U.S.S.R.). The isotherms are very similar to those of erionite reported by Chelishchev and Volodin (1977). The results show that phillipsite is selective for Cs^+ , Rb^+ , and K^+ , but not for Li^+ . The selectivity series for phillipsite determined by Chelishchev et al. (1984) is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. The equilibrium constants reported by the authors and the Gibbs free energies calculated from those values are listed in Table 9.

Thermodynamic parameters derived by Ames (1964a,b) for Na^+/K^+ , Cs^+/Na^+ , Cs^+/K^+ , $\text{Ca}^{2+}/\text{Na}^+$, $\text{Sr}^{2+}/\text{Ca}^{2+}$, and $\text{Sr}^{2+}/\text{Na}^+$ exchange on phillipsite are also included in Table 9. The isotherm experiments by Ames (1964a,b) used a phillipsite material (90% or higher in purity; CEC equal to 2.3 meq/g) from Pine Valley, Nevada, and were conducted at 298 K and 0.1 N solution concentration.

APPLICATION OF THERMODYNAMIC MODELS

As noted in a previous section, thermodynamic models provide systematic bases for understanding ion-exchange behavior and serve as tools for predicting exchange equilibria under conditions not previously studied. Several examples are presented in this section to illustrate the use of an ion-exchange model, based on the Margules equation for

Table 9. Literature values of equilibrium constants and Gibbs free energies for ion-exchange reactions involving phillipsite.

Ion-Exchange Reaction	$\ln K_{(A,B)}$	$\Delta G_{(A,B)}^{\circ}$ (kJ/mol)*	Reference	Remarks
$\text{Li}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{LiL}$	-2.60	6.38	Chelishchev et al. (1984)	T = 295 K; phillipsite from Georgia (of the former U.S.S.R.)
$\text{Na}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{NaL}$	-1.66	4.1	Ames (1964a)	T = 298 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{K}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{KL}$	2.90	-7.11	Chelishchev et al. (1984)	T = 295 K; phillipsite from Georgia (of the former U.S.S.R.)
$\text{Rb}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{RbL}$	3.54	-8.68	Chelishchev et al. (1984)	T = 295 K; phillipsite from Georgia (of the former U.S.S.R.)
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	4.01	-9.84	Chelishchev et al. (1984)	T = 295 K; phillipsite from Georgia (of the former U.S.S.R.)
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	2.82	-7.0	Adabbo et al. (1999)	T = 298 K; synthetic phillipsite; CEC = 3.60 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	0.83	-2.1	Adabbo et al. (1999)	T = 298 K; hydrothermal phillipsite from Vesuvius, Italy; CEC = 4.71 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	3.27	-8.1	Adabbo et al. (1999)	T = 298 K; sedimentary phillipsite from Marano, Italy; CEC = 3.55 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	3.27	-8.1	Ames (1964a)	T = 298 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{Cs}^+ + \text{NaL} \Leftrightarrow \text{Na}^+ + \text{CsL}$	2.59	-7.4	Ames (1964a)	T = 343 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{Cs}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{CsL}$	1.67	-4.1	Ames (1964a)	T = 298 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{Cs}^+ + \text{KL} \Leftrightarrow \text{K}^+ + \text{CsL}$	1.61	-4.6	Ames (1964a)	T = 343 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{Ca}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CaL}_2$	-1.81	4.5	Ames (1964b)	T = 298 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-2.66	6.6	Adabbo et al. (1999)	T = 298 K; synthetic phillipsite; CEC = 3.60 meq/g

$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-0.97	2.4	Adabbo et al. (1999)	T = 298 K; hydrothermal phillipsite from Vesuvius, Italy; CEC = 4.71 meq/g
$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-1.97	4.8	Adabbo et al. (1999)	T = 298 K; sedimentary phillipsite from Marano, Italy; CEC = 3.55 meq/g
$\text{Sr}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{SrL}_2$	-2.23	5.5	Ames (1964b)	T = 298 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{Sr}^{2+} + \text{CaL}_2 \Leftrightarrow \text{Ca}^{2+} + \text{SrL}_2$	-0.53	1.3	Ames (1964b)	T = 298 K; Pine Valley, Nevada phillipsite; CEC = 2.3 meq/g
$\text{Pb}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{ZnL}_2$	3.13	-7.8	Pansini et al. (1996)	T = 298 K; phillipsite from Chiaiano, Naples, Italy; CEC = 3.3 meq/g
$\text{Pb}^{2+} + 2\text{KL} \Leftrightarrow 2\text{Na}^+ + \text{PbL}_2$	-1.7	4.2	Pansini et al. (1996)	T = 298 K; phillipsite from Chiaiano, Naples, Italy; CEC = 3.3 meq/g
$\text{Cd}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{CdL}_2$	-3.7	9.2	Colella et al. (1998)	T = 298 K
$\text{Zn}^{2+} + 2\text{NaL} \Leftrightarrow 2\text{Na}^+ + \text{ZnL}_2$	-5.29	13.1	Colella et al. (1998)	T = 298 K; phillipsite from Marano, Italy; CEC = 3.3C

*Values from Adabbo et al. (1999), Pansini et al. (1996), and Colella et al. (1998), given in kilojoules per equivalent, were converted to kilojoules per mole. The $\Delta G_{(A,B)}^\circ$ values listed for Chelishchev et al. (1984) were calculated from the equilibrium constants reported in the reference.

zeolite solid solutions and the Pitzer equations for aqueous-phase activity coefficients, to represent and predict ion-exchange equilibria. The examples focus on clinoptilolite, for which selected sets of experimental data taken from the literature were used to derive parameters for the Margules equation and to calculate ion-exchange isotherms as functions of solution composition and concentration. Where ion-exchange data are available, calculated values are compared with measured values. The ion-exchange model also was used to predict cation concentrations in the aqueous solution based on the composition of the zeolite in equilibrium with the solution.

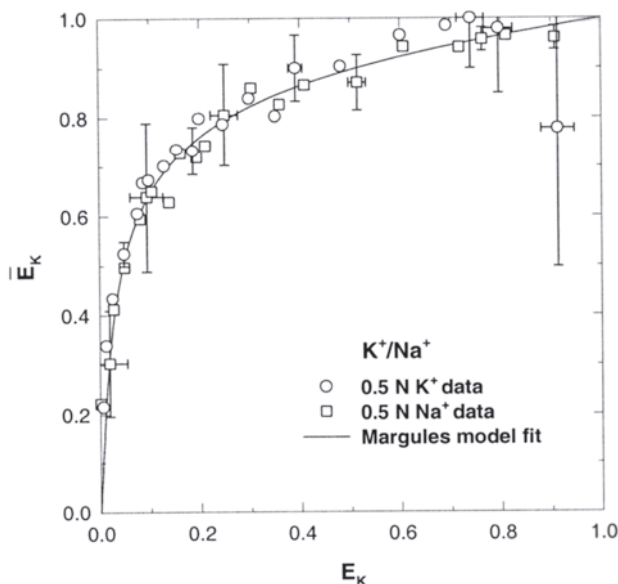
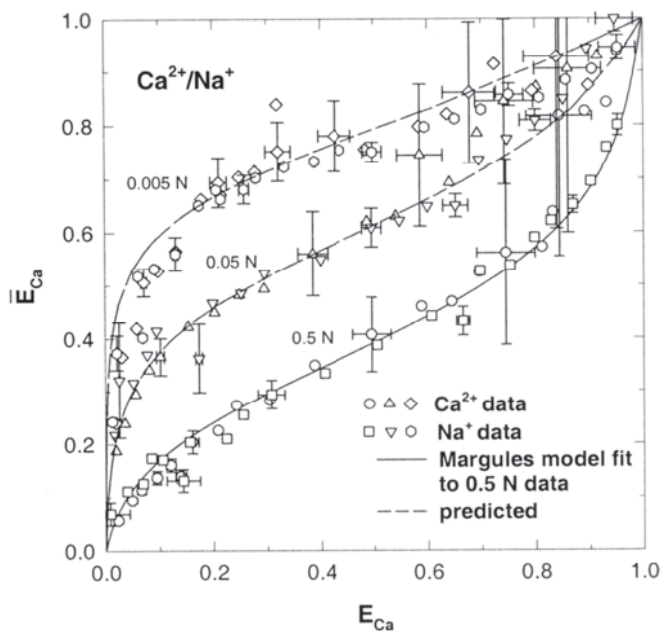


Figure 5. Isotherm data for ion exchange at 298 K between clinoptilolite and K^+/Na^+ solutions (0.5 N; Cl^- anion). Circles and squares were calculated from solution concentrations of K^+ and Na^+ , respectively. Some error bars, based on K^+ and Na^+ analytical uncertainties, are shown. The curve was fit to the isotherm data using a Margules solid-solution model. Data are from Pabalan (1994).

Figure 6. Isotherm data for ion exchange at 298 K between clinoptilolite and Ca^{2+}/Na^+ solutions (0.005, 0.05, and 0.5 N; Cl^- anion). The isotherm points were calculated from solution concentrations of Ca^{2+} or Na^+ . Some error bars, based on Ca^{2+} and Na^+ analytical uncertainties, are shown. The solid curve was fit to the 0.50 N isotherm data using a Margules solid-solution model. The dashed curves represent predicted values. Data are from Pabalan (1994).



Margules model parameters

Values of $\ln K_{v(A,B)}$ versus \bar{X}_A were calculated from isotherm data on clinoptilolite for the exchange couples K^+/Na^+ , Ca^{2+}/Na^+ , Sr^{2+}/Na^+ , Sr^{2+}/K^+ , and Ca^{2+}/K^+ taken from the studies of Pabalan (1994) and Pabalan and Bertetti (1999). The isotherm data are shown in Figures 3 to 8, and, as examples, $\ln K_{v(A,B)}$ versus \bar{X}_A for two systems, Sr^{2+}/Na^+ and Sr^{2+}/K^+ , are plotted in Figures 9 and 10. Using the calculated values of $\ln K_{v(A,B)}$ versus \bar{X}_A , Equation (25) was used to derive the ion-exchange equilibrium constant,

Figure 7. Isotherm data for ion exchange at 298 K between clinoptilolite and $\text{Ca}^{2+}/\text{K}^+$ solutions (0.05 N; Cl^- anion). Circles and squares were calculated from Ca^{2+} and K^+ analytical data, respectively. Some error bars, based on Ca^{2+} and K^+ analytical uncertainties, are shown. The curve was fit to the isotherm data using a Margules solid-solution model. Data are from Pabalan and Bertetti (1999).

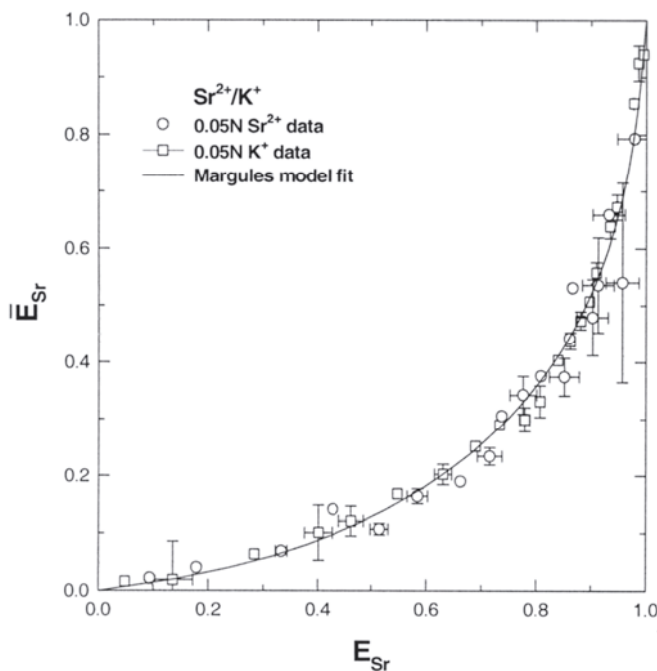
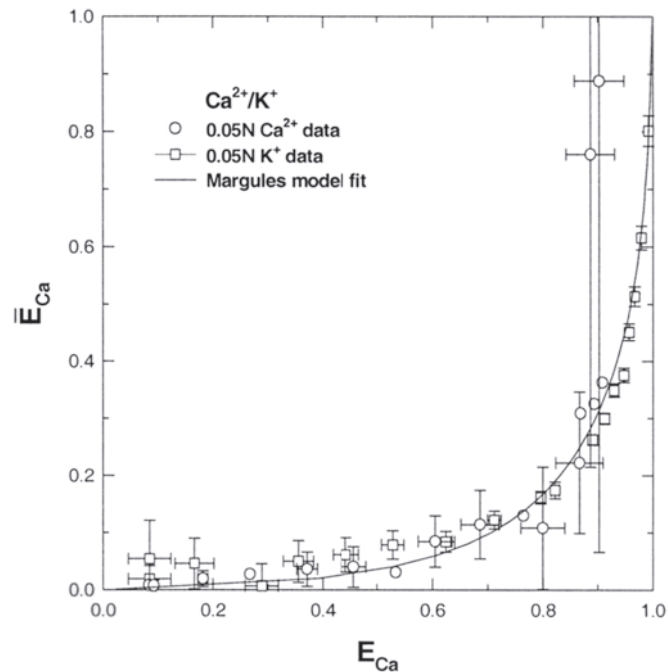


Figure 8. Isotherm data for ion exchange at 298 K between clinoptilolite and $\text{Sr}^{2+}/\text{K}^+$ solutions (0.05 N; Cl^- anion). Circles and squares were calculated from Sr^{2+} and K^+ analytical data, respectively. Some error bars, based on Sr^{2+} and K^+ analytical uncertainties, are shown. The curve was fit to the isotherm data using a Margules solid-solution model. Data from Pabalan and Bertetti (1999).

$K_{(A,B)}$, and the Margules parameters, W_A and W_B . In the regression, $\ln K_{v(A,B)}$ was weighted inversely proportional to the square of its estimated overall uncertainty (Pabalan 1994). Where data at different total solution concentrations are available, data at only one solution concentration were used in the regression, and data at other concentrations were used to check model predictions. The derived equilibrium constants and Margules parameters are listed in Table 10. The solid curves in Figures 3 to 8, as well as in Figures 9 and 10, represent the Margules model fits to the isotherm data.

Experimental data for $\text{NH}_4^+/\text{Na}^+$ exchange at 0.1 N total solution concentration from Townsend and Loizidou (1984) and Jama and Yucel (1990) were used to calculate $\ln K_{v(\text{NH}_4, \text{Na})}$ versus \bar{X}_{NH_4} and to derive the equilibrium constant and Gibbs free energy for the exchange reaction (Table 10). As discussed in a previous section, both sets of authors

Figure 9. Vanselow selectivity coefficient, $\ln K_{v(Sr,Na)}$, versus cationic mole fraction, \bar{X}_{Sr} , calculated from the 0.05 N Sr^{2+}/Na^+ isotherm data on clinoptilolite. Circles and squares were calculated from Sr^{2+} and Na^+ data, respectively. The curve represents the best fit of the Margules model to the 0.05 N data. Figure taken from Pabalan and Bertetti (1999).

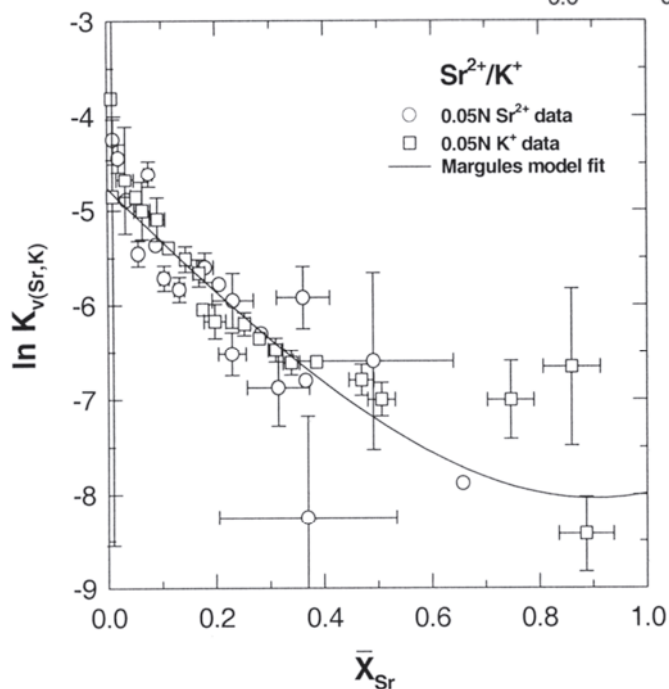
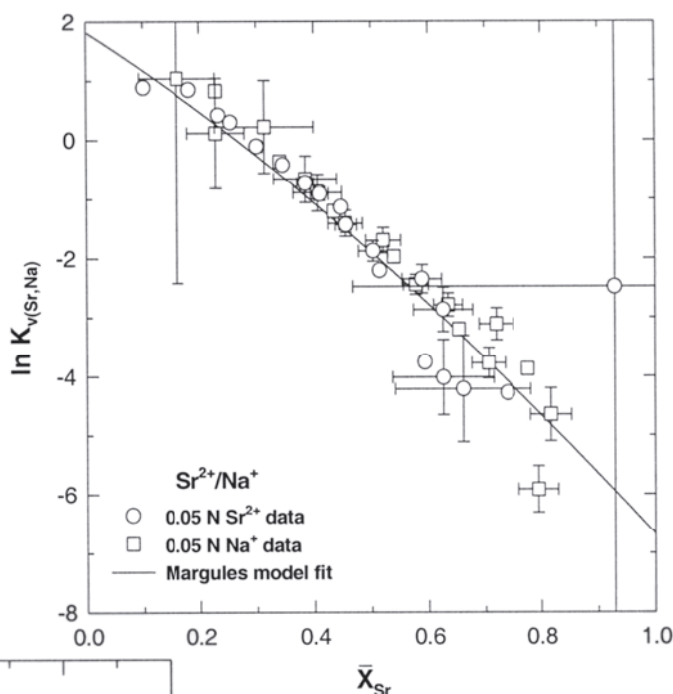


Figure 10. Vanselow selectivity coefficient, $\ln K_{v(Sr,K)}$, versus cationic mole fraction, \bar{X}_{Sr} , calculated from the 0.05 N Sr^{2+}/K^+ isotherm data on clinoptilolite. Circles and squares were calculated from Sr^{2+} and K^+ data, respectively. The curve represents the best fit of the Margules model to the 0.05 N data. Figure taken from Pabalan and Bertetti (1999).

observed incomplete exchange of NH_4^+ for Na^+ , and the isotherm data were therefore normalized to the reported $\bar{E}_{NH_4,max}$ before the thermodynamic parameters were derived. The original C and normalized C NH_4^+/Na^+ isotherm points from the two references are plotted in Figure 11a. The solid curve in Figure 11a represents the best-fit of the Margules model to the two sets of data. Experimental data from White (1988), also at 0.1 N, are compared in Figure 11b with the isotherm calculated from the model. There is very good agreement between experimental and calculated values.

Data on NH_4^+/K^+ ion exchange at 0.1 N total solution concentration from Jama and Yucel (1990) are plotted in Figure 12. These data were normalized to the reported $\bar{E}_{NH_4,max}$ of 0.50 and were used to derive the equilibrium constant and Gibbs free energy for the exchange reaction (Table 10). The isotherms calculated from the model compare well with experimental data, as shown in Figure 12.

Table 10. Values of Margules parameters, equilibrium constants, and Gibbs free energies of ion exchange derived from isotherm data*

Cations (A,B)	W_A	W_B	$\ln K_{(A,B)}$	$\Delta G_{(A,B)}^\circ$ (kJ/mol)	Reference
K^+, Na^+	-0.989	-1.41	3.22±0.03	-7.98±0.08	Pabalan (1994)
Cs^+, Na^+	-1.62	-1.45	4.30±0.24	-10.7±0.6	this study
Li^+, Na^+	-0.52	-0.88	-2.12±0.07	5.26±0.18	this study
NH_4^+, Na^+	-0.51	-0.58	1.64±0.05	-4.07±0.13	this study
Ca^{2+}, Na^+	-2.67	-1.22	-1.65±0.08	4.09±0.20	Pabalan (1994)
Sr^{2+}, Na^+	-2.68	-3.27	-1.14±0.07	2.83±0.18	Pabalan and Bertetti (1999)
Cs^+, K^+	-1.83	-0.706	1.04±0.12	-2.58±0.30	this study
NH_4^+, K^+	-0.324	-0.496	-0.645±0.173	1.60±0.43	this study
Ca^{2+}, K^+	-2.02	-0.591	-8.50±0.18	21.1±0.5	Pabalan and Bertetti (1999)
Sr^{2+}, K^+	-1.75	-0.731	-6.52±0.10	16.2±0.3	Pabalan and Bertetti (1999)

* W_A, W_B and $\ln K_{(A,B)}$ were derived from weighted regression of Equation (25) to the $\ln K_{v(A,B)}$ versus \bar{X}_A data. The 1σ errors in $\ln K_{(A,B)}$ and $\Delta G_{(A,B)}^\circ$ are also listed.

Isotherm data from Ames (1964a), Howery and Thomas (1965), and Chelishchev et al. (1973), plotted in Figure 13, were used to derive the thermodynamic parameters listed in Table 10 for Cs^+/Na^+ exchange on clinoptilolite. As discussed earlier, homovalent cation exchange is not significantly affected by variations in total solution concentration. One reason for this is the minor variation in solution activity coefficient ratios for homovalent exchange reactions over a large concentration range (e.g. 0.0005 N to 1.0 N). Therefore, isotherm data for homovalent exchanges, like the Cs^+/Na^+ system, collected at different total solution concentrations can be expected to be very similar. However, as seen in Figure 13, data from several investigators exhibit a greater than expected variability, possibly due to differences in the clinoptilolite samples and in the experimental protocols.

One way of dealing with variability in data between different studies is to use all the available data to generate a single model regression to represent the system isotherm. The solid curve in Figure 13 represents the best-fit of the Margules model to all isotherm data from the three Cs^+/Na^+ studies. The Margules fit not only does an adequate job of representing the ‘average’ Cs^+/Na^+ exchange isotherm, but it also captures the variability of data between experiments. Curves representing model calculations that account for 2σ uncertainties in $\ln K_{(Cs,Na)}$ alone (dashed lines) or in all model parameters ($\ln K_{(Cs,Na)}$, W_{Cs} , and W_{Na}) (dotted lines) are also plotted in the figure. Note that the isotherms accounting for the $\pm 2\sigma$ variation in parameter uncertainty capture the variability of data

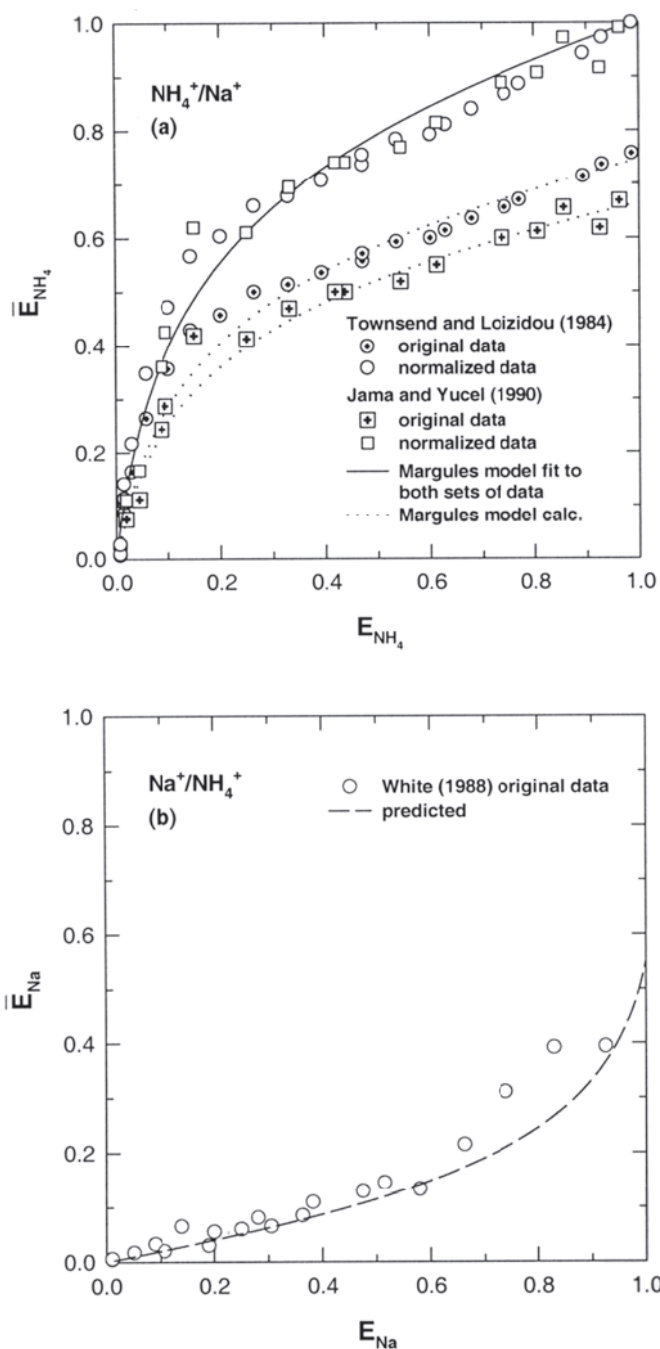


Figure 11. Isotherm data for ion exchange between clinoptilolite and 0.1 N $\text{NH}_4^+/\text{Na}^+$ solutions. The data from Townsend and Loizidou (1984) and Jama and Yucel (1990), plotted in Figure 11a, were normalized and regressed to derive the equilibrium constant and Margules parameters. A comparison of the calculated isotherm with data from White (1988) is shown in Figure 11b.

in the three experiments. Thus, although it is difficult to determine which of the three sets of experiments is 'correct,' the 2σ uncertainties in the Margules model parameters adequately represent the uncertainties that arise due to differences among experiments. Therefore, bounding isotherms can be generated where uncertainty due to inter-laboratory variability is high.

Experimental results from Chelishchev et al. (1973) on the binary system Li^+/Na^+ are plotted in Figure 14. The Margules model (solid curve) fits the isotherm data well. Data on K^+/Cs^+ exchange from Chelishchev et al. (1973) and Ames (1968) are plotted in Figure 15. The two data sets do not agree well, even considering the difference in total solution concentration. The Margules model could fit either data set equally well but would result in different thermodynamic parameters. For the purposes of this study, the model was fit to both sets of isotherm data. The derived equilibrium constants and Gibbs

Figure 12. Isotherm data for ion exchange between clinoptilolite and 0.1 N NH_4^+/K^+ solutions. Data from Jama and Yucel (1990) were normalized and regressed to derive the equilibrium constant and Margules parameters.

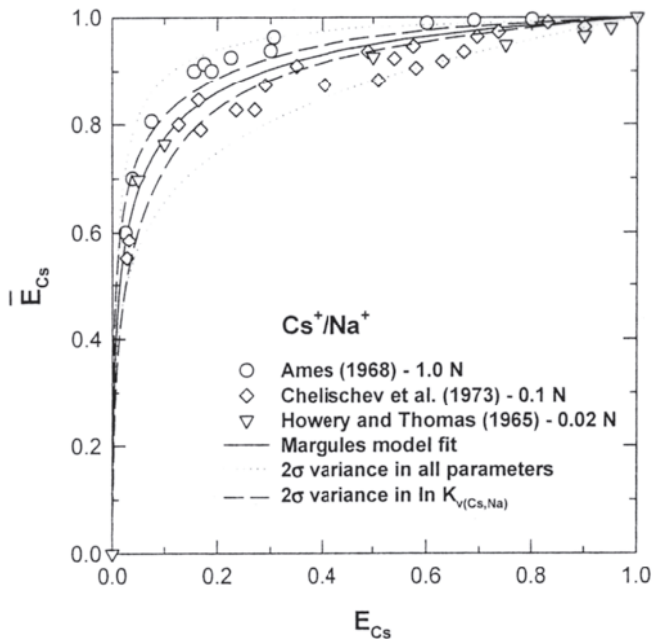
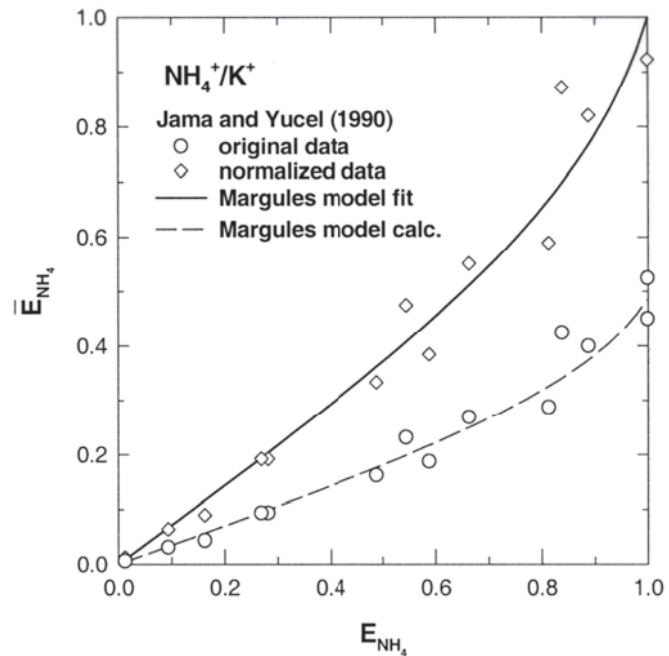


Figure 13. Isotherm data for ion exchange between clinoptilolite and Cs^+/Na^+ solutions. Data from Ames (1964a), Chelishchev et al. (1973), and Howery and Thomas (1965) were regressed to derive the equilibrium constant and Margules parameters. The solid curve is the best fit to all the isotherm data. The dashed curves represent model calculations in which $\ln K_{(\text{Cs},\text{Na})}$ was varied between its $\pm 2\sigma$ variance. The dotted curves represent model calculations in which all model parameters [$\ln K_{(\text{Cs},\text{Na})}$, W_{Cs} , and W_{Na}] were varied between their $\pm 2\sigma$ variance. The $\pm 2\sigma$ isotherm envelope is able to represent data variation among different studies.

free energies for Li^+/Na^+ and K^+/Cs^+ exchange are listed in Table 10.

Excess Gibbs energies calculated from the Margules parameters and Equation (23) for several binary clinoptilolite solid solutions are plotted in Figures 16 and 17. These figures illustrate the relative deviation from ideal behavior of the zeolite solid solutions. All the systems studied exhibit some degree of nonideal behavior. Where the degree of nonideality is not large, the solid phase activity coefficients are close to 1.0 and the activities of the zeolite components can be approximated by their mole fraction (i.e. $\bar{a}_i \approx \bar{X}_i$). For example, Figure 16 indicates that the nonideality for the $\text{NH}_4^+/\text{Na}^+$ system is relatively small, with a maximum of -0.34 kJ/mol. Figure 18 compares $\text{NH}_4^+/\text{Na}^+$ ion exchange data (shown previously in Fig. 11) with isotherms calculated either using the Margules model, i.e. explicitly accounting for nonideal behavior, or assuming an ideal solid solution. The comparison shows that, for this particular case, the data can be

Figure 14. Isotherm data for ion exchange between clinoptilolite and Li^+/Na^+ solutions. Data from Chelishchev et al. (1973) were regressed to derive the equilibrium constant and Margules parameters. The solid curve is the best fit to the isotherm data.

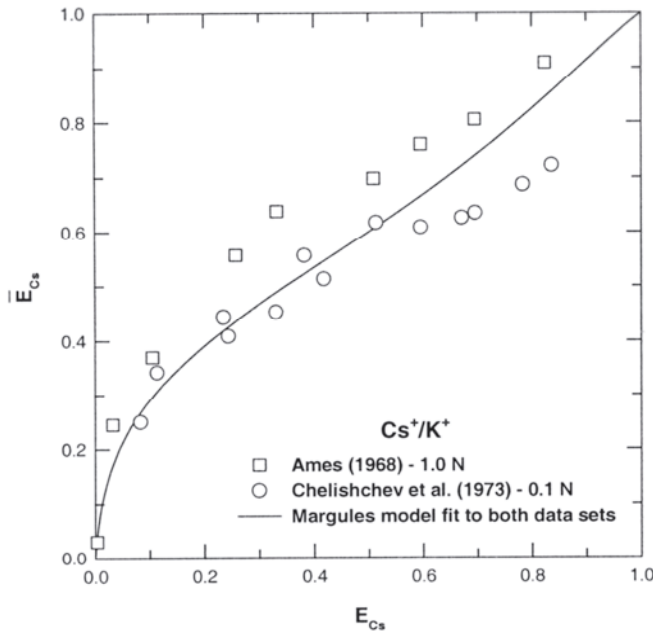
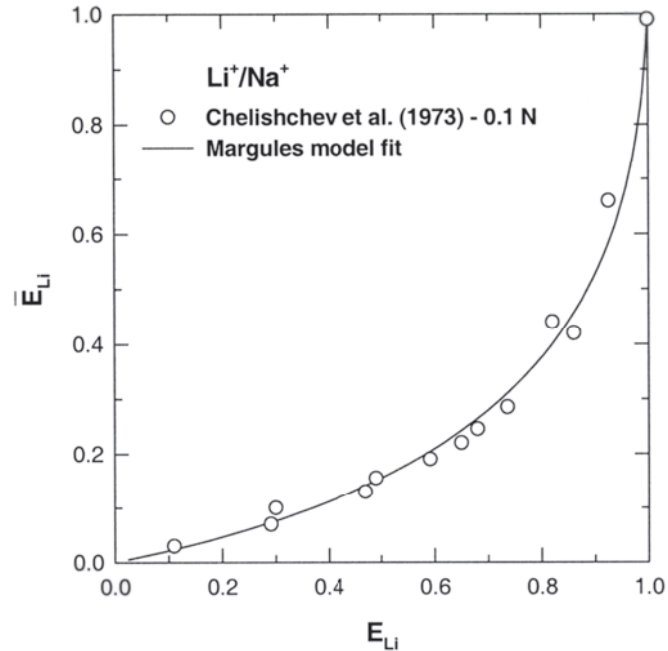


Figure 15. Isotherm data for ion exchange between clinoptilolite and K^+/Cs^+ solutions. Data from Ames (1968) and Chelishchev et al. (1973) were regressed to derive the equilibrium constant and Margules parameters. The solid curve is the best fit to both sets of isotherm data.

adequately represented by an ideal solid solution model. In contrast, Figure 16 indicates that the $\text{Sr}^{2+}/\text{Na}^+$ system is highly nonideal. The $\text{Sr}^{2+}/\text{Na}^+$ isotherm calculated without explicitly accounting for nonideality effects, shown in Figure 19, agrees poorly with experimental data.

Isotherms as functions of solution composition and concentration

Thermodynamic models facilitate the calculation of ion-exchange equilibria, particularly for exchange involving heterovalent cations for which the isotherm shapes depend strongly on the total solution concentration. From the known ion-exchange equilibrium constant, $K_{(A,B)}$, and Margules solid solution parameters, W_A and W_B , values of $K_{v(A,B)}$ can be calculated for a given zeolite composition, \bar{X}_A , using Equation (25). If the total solution normality is known and aqueous activity coefficients can be calculated,

Figure 16. Excess Gibbs energy, \bar{G}^E , for $(\text{NH}_4^+, \text{Na}^+)$ -, $(\text{Li}^+, \text{Na}^+)$ -, $(\text{K}^+, \text{Na}^+)$ -, $(\text{Cs}^+, \text{Na}^+)$ -, $(\text{Ca}^{2+}, \text{Na}^+)$ -, and $(\text{Sr}^{2+}, \text{Na}^+)$ -clinoptilolite solid solutions calculated using Equation (23) and the Margules parameters listed in Table 10.

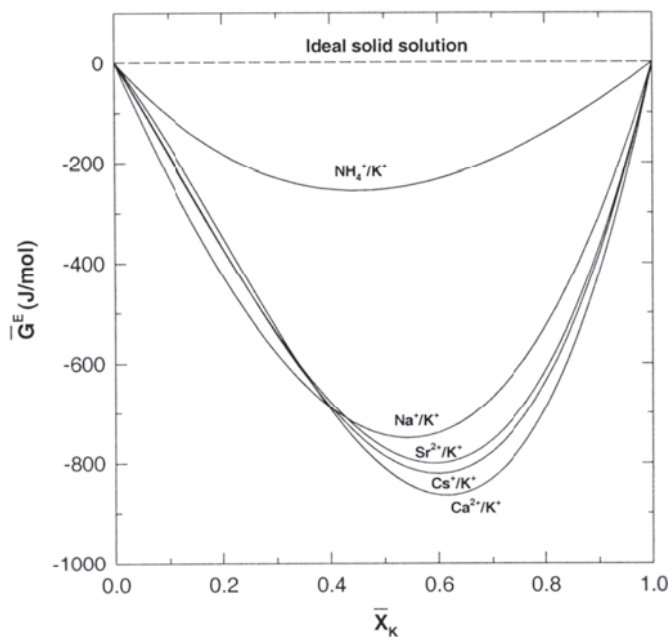
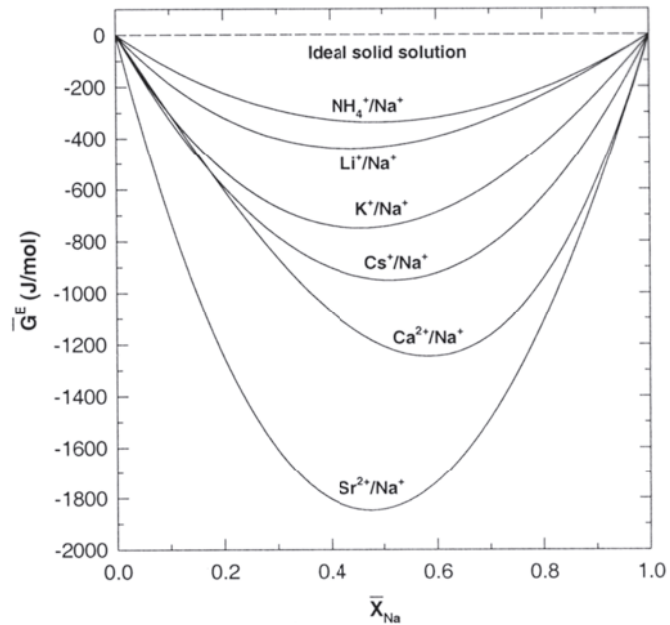


Figure 17. Excess Gibbs energy, \bar{G}^E , for $(\text{Cs}^+, \text{K}^+)$ -, $(\text{Na}^+, \text{K}^+)$ -, $(\text{NH}_4^+, \text{K}^+)$ -, $(\text{Ca}^{2+}, \text{K}^+)$ - and $(\text{Sr}^{2+}, \text{K}^+)$ -clinoptilolite solid solutions calculated using Equation (23) and the Margules parameters listed in Table 10.

then the composition of the aqueous solution in equilibrium with the zeolite can be solved from Equation (13). Isotherm values for the exchange couples $\text{Sr}^{2+}/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ predicted using the Margules model (dashed curves) are compared in Figures 3 and 6 with experimental data. The figures show very good agreement between measured and calculated values.

Figures 20, 21, 22, and 23 show isotherms for ion exchange involving $\text{Ca}^{2+}/\text{Na}^+$, $\text{Sr}^{2+}/\text{Na}^+$, $\text{Sr}^{2+}/\text{K}^+$, and $\text{Ca}^{2+}/\text{K}^+$ mixtures, respectively, and clinoptilolite as functions of total solution concentration. The isotherms were calculated using Margules parameters derived from the isotherm data of Pabalan (1994) and Pabalan and Bertetti (1999). Isotherm data from other sources are also plotted for comparison. Data from Ames (1964b) on $\text{Sr}^{2+}/\text{Na}^+$ exchange at 1.0 N agree well with the calculated isotherm (Fig. 21), although his data on $\text{Ca}^{2+}/\text{Na}^+$ do not agree as well with the calculated values (Fig. 20).

Figure 18. The symbols are normalized $\text{NH}_4^+/\text{Na}^+$ isotherm data from Figure 11(a). The solid curve is the isotherm calculated using the Margules model. The dotted curve is the isotherm calculated assuming that $(\text{NH}_4^+/\text{Na}^+)$ -clinoptilolite behaves as an ideal solid solution.

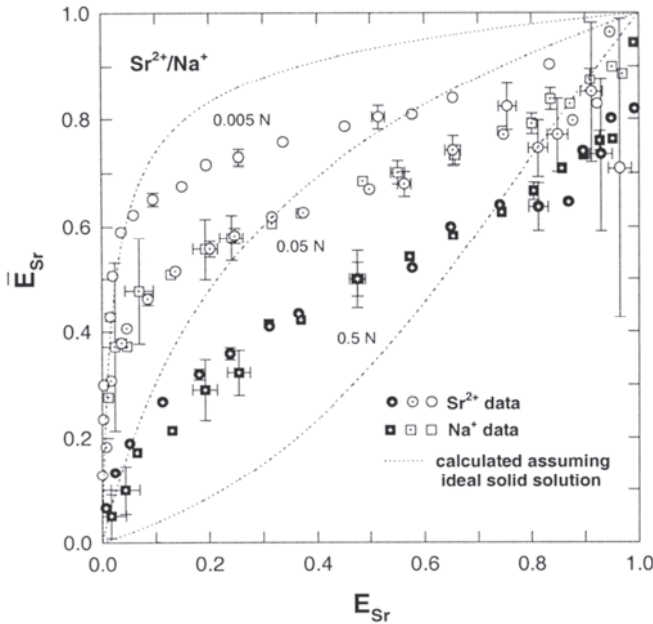
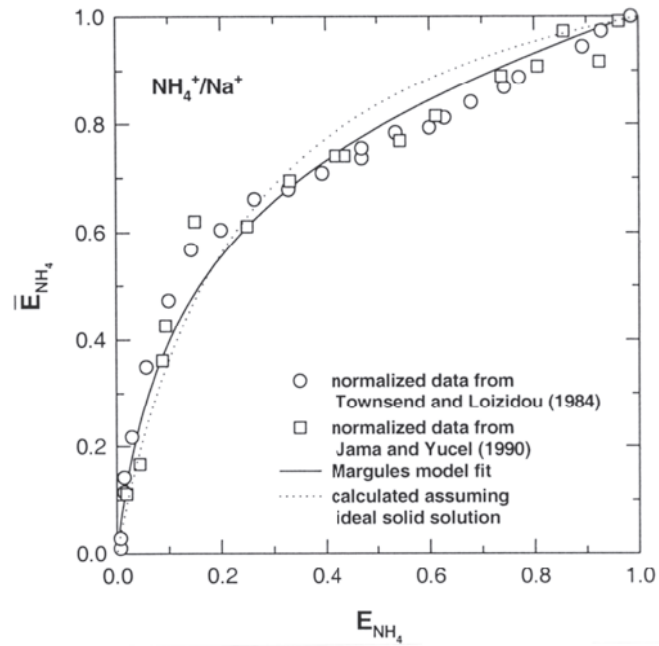


Figure 19. $\text{Sr}^{2+}/\text{Na}^+$ isotherm data (shown by symbols; taken from Fig. 3) compared with isotherms (shown by dotted lines) calculated assuming that $(\text{Sr}^{2+},\text{Na}^+)$ -clinoptilolite behaves as an ideal solid solution.

Values of \bar{E}_{Sr} from Chelishchev et al.'s (1973) $\text{Sr}^{2+}/\text{Na}^+$ isotherm points are lower than the calculated values (Fig. 21), whereas \bar{E}_{Ca} values from White's (1988) $\text{Ca}^{2+}/\text{K}^+$ data, which show quite a bit of scatter, are generally higher than the calculated values (Fig. 23).

Isotherms change little with a change in solution concentration for homovalent exchange reactions. For example, in Figure 24, the K^+/Na^+ isotherm calculated for a solution concentration of 1.0 N is essentially the same as the isotherm at 0.005 N. Comparison of calculated values with experimental data from Ames (1964a) at 1.0 N and from White (1988) at 0.1 N shows good agreement.

Aqueous composition calculated from zeolite analysis

An interesting application of ion-exchange models is the calculation of groundwater

Figure 20. Isotherms for ion exchange between clinoptilolite and aqueous solutions of $\text{Ca}^{2+}/\text{Na}^{+}$ from 0.0005 to 1.0 N calculated using Margules parameters derived from the 0.50 N isotherm data. Also shown are isotherm data at 1.0 N from Ames (1964b).

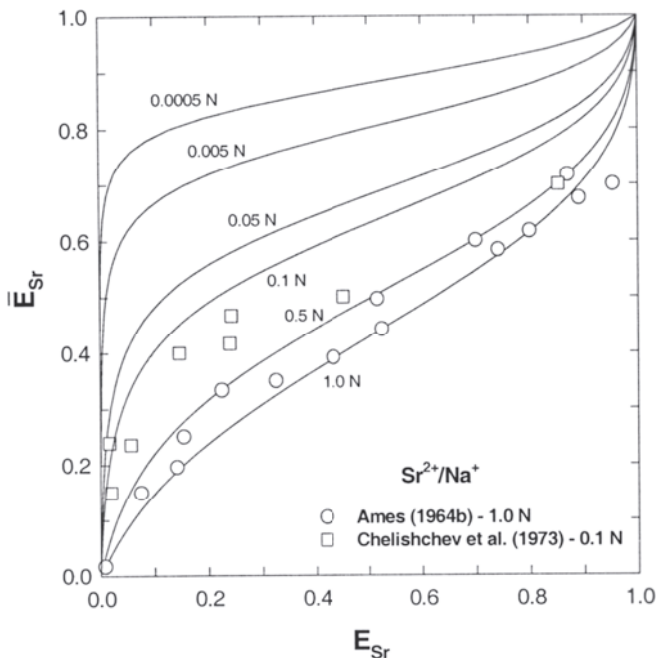
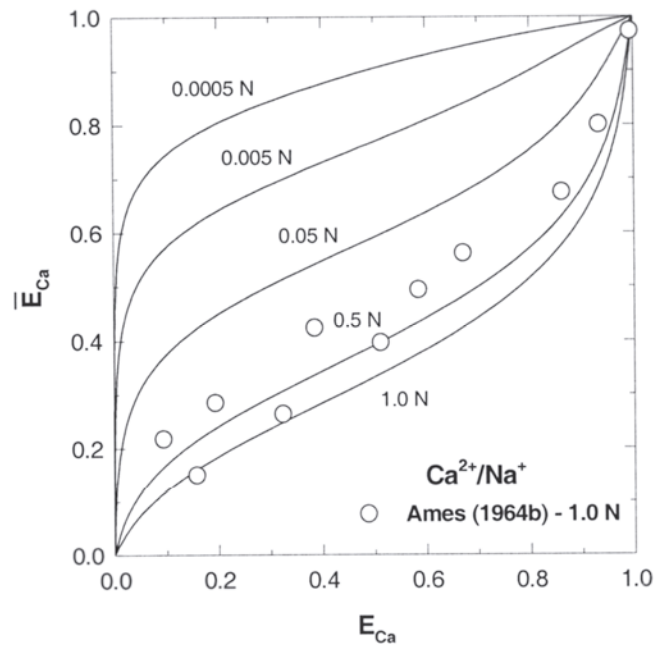


Figure 21. Isotherms for ion exchange between clinoptilolite and aqueous solutions of $\text{Sr}^{2+}/\text{Na}^{+}$ from 0.0005 to 1.0 N calculated using Margules parameters derived from the 0.05 N isotherm data. Also shown are isotherm data at 1.0 N from Ames (1964b) and at 0.1 N from Chelishchev et al. (1973).

composition based on analytical data on the coexisting zeolite phase (Pabalan and Bertetti 1999). For example, it is difficult to obtain samples of groundwater from hydrologically unsaturated rock units, such as those surrounding the potential nuclear waste geologic repository at Yucca Mountain, Nevada. Although efforts have been made to extract aqueous solutions by high-pressure triaxial compression of Yucca Mountain rock samples (Yang et al. 1988, 1996; Peters et al. 1992), there are large variabilities in the chemical composition of solutions derived using this technique and some rock samples do not yield sufficient water for chemical analysis. Aqueous samples have also been extracted from unsaturated soils and sands using ultracentrifugation techniques (Edmunds et al. 1992; Puchelt and Bergfeldt 1992). It is uncertain whether compositions of water extracted from rock pores by ultracentrifugation or by high-pressure squeezing methods accurately represent the compositions of *in situ* water. Water extracted by these methods may have compositions different from those of *in situ* water due to several possible processes

(Peters et al. 1992): (1) dilution of pore solutions by water desorbed from hydrated minerals like zeolites and clays; (2) dissolution reactions due to increased mineral solubility and/or higher carbon dioxide concentration at higher pressures; (3) membrane filtration by clays and zeolites; and (4) ion exchange with zeolites and clays.

Thermodynamic models for ion-exchange equilibria may help reduce uncertainties associated with sampling and analysis of groundwater in unsaturated stratigraphic horizons by constraining the water cation chemistry. Data from analysis of zeolite composition, such as those derived by electron microprobe techniques, combined with estimates of the total normality of the aqueous phase, can be used to calculate cation concentrations in the groundwater. Ideally, the zeolite sample should be obtained by dry coring methods to minimize altering its composition. The ability of thermodynamic models to estimate the cationic composition of the aqueous phase based on the chemical composition of the zeolite is evaluated in this section.

Figure 22. Isotherms for ion exchange between clinoptilolite and aqueous solutions of $\text{Sr}^{2+}/\text{K}^+$ from 0.00005 to 1.0 N calculated using Margules parameters derived from the 0.05 N isotherm data.

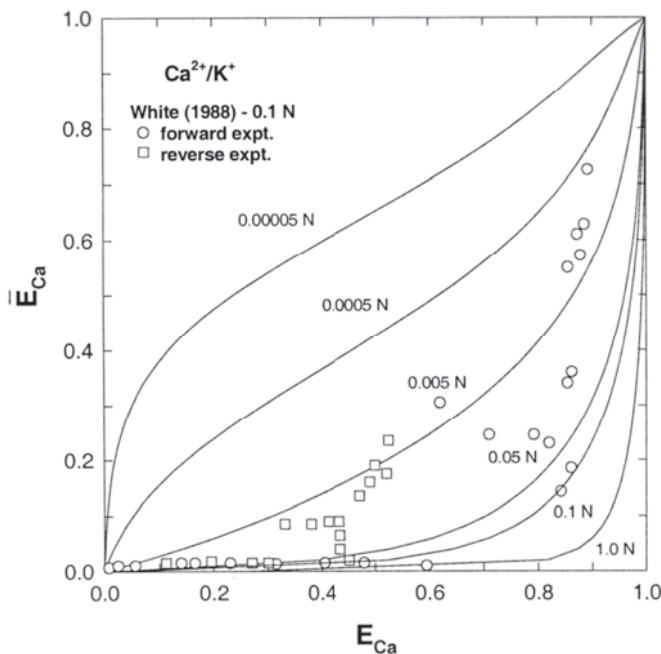
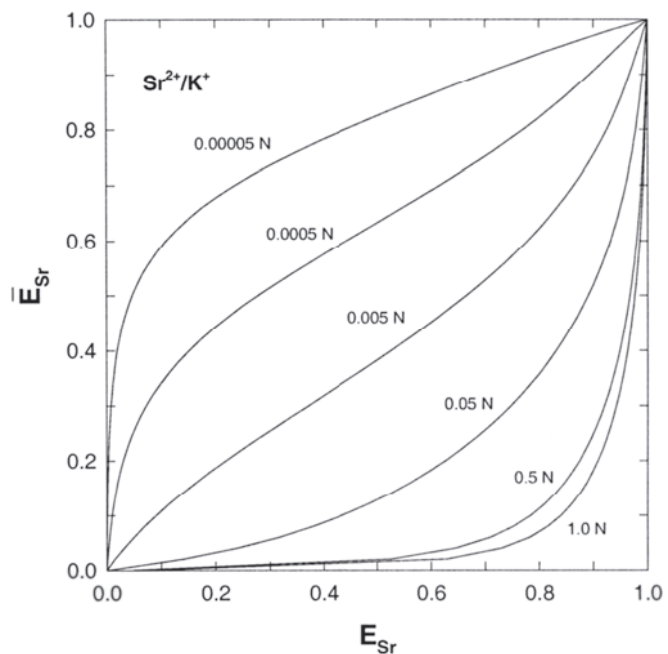
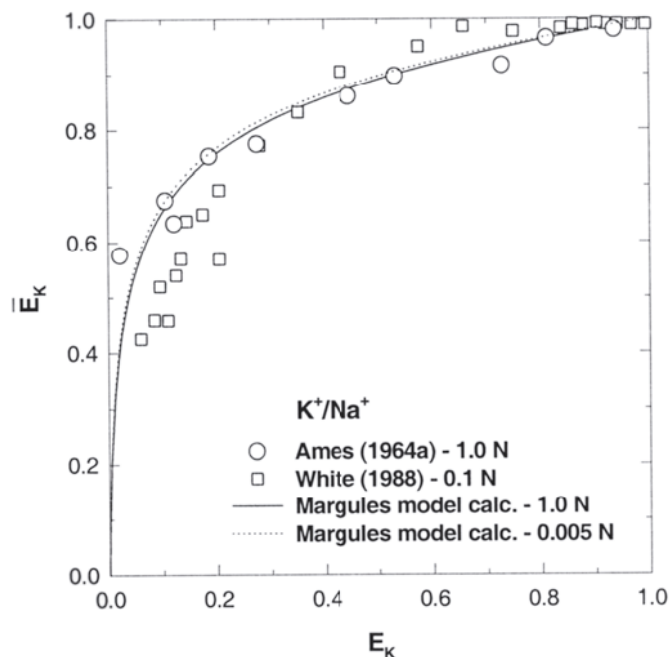


Figure 23. Isotherms for ion exchange between clinoptilolite and aqueous solutions of $\text{Ca}^{2+}/\text{K}^+$ from 0.00005 to 1.0 N calculated using Margules parameters derived from the 0.05 N isotherm data. Also plotted are isotherm data at 0.1 N from White (1988).

Figure 24. Isotherms for ion exchange between clinoptilolite and K^+/Na^+ calculated from 0.005 N and 1.0 N solution concentration using Margules parameters derived from the 0.5 N isotherm. Data. Also plotted are isotherm data at 1.0 N from Ames (1964a) and at 0.1 N from White (1988).



Equations for calculating solution composition from zeolite data. The ratio of the aqueous activities of two cations, A^{z_A+} and B^{z_B+} , participating in an ion-exchange reaction such as that represented by Equation (1) can be written as

$$\frac{(a_B)^{z_A}}{(a_A)^{z_B}} = \frac{(M_B)^{z_A} (?_B)^{z_A}}{(M_A)^{z_B} (?_A)^{z_B}} = K_{v(A,B)} \frac{(\bar{X}_B)^{z_A}}{(\bar{X}_A)^{z_B}} \quad (30)$$

Substituting $K_{v(A,B)}$ from Equation (25) and writing the zeolite composition in terms of \bar{X}_A only, the aqueous activity ratio can be represented in terms of $K_{(A,B)}$, W_A , and W_B as

$$\frac{(a_B)^{z_A}}{(a_A)^{z_B}} = \frac{(1 - \bar{X}_A)^{z_A}}{(\bar{X}_A)^{z_B}} \exp \left\{ \ln K_{(A,B)} + z_A \bar{X}_A^2 [W_B + 2(1 - \bar{X}_A)(W_A - W_B)] - z_B (1 - \bar{X}_A)^2 [W_A + 2\bar{X}_A(W_B - W_A)] \right\} \quad (31)$$

Because the total normality of a binary aqueous solution, TN, can be calculated from

$$TN = z_A M_A + z_B M_B \quad , \quad (32)$$

the ratio of the molarities of A^{z_A+} and B^{z_B+} can be written in terms of the molarity of either A^{z_A+} only or B^{z_B+} only. Thus,

$$\frac{(M_B)^{z_A}}{(M_A)^{z_B}} = \frac{[(TN - z_A M_A)/z_B]^{z_A}}{(M_A)^{z_B}} = \frac{(a_B)^{z_A} (\gamma_A)^{z_B}}{(a_A)^{z_B} (\gamma_B)^{z_A}} \quad (33)$$

For binary ion-exchange reactions involving monovalent cations ($z_A = z_B = 1$), one can derive from Equation (33) expressions for M_A and M_B that are fairly simple:

$$M_A = \frac{TN}{(1 + k)} \quad ; \quad M_B = TN - M_A \quad (34)$$

where

$$k = \frac{(a_B)^{z_A} (\gamma_A)^{z_B}}{(a_A)^{z_B} (\gamma_B)^{z_A}} \quad (35)$$

For exchange reactions where $z_A = 2$ and $z_B = 1$, the solution compositions can be solved using the quadratic formula

$$M_A = \frac{-c \pm \sqrt{c^2 - 4bd}}{2b} ; M_B = TN - 2M_A \quad (36)$$

where

$$b = 1; c = \frac{-4TN - k}{4} ; d = \left(\frac{TN}{2}\right)^2 \quad (37)$$

Using Equations (31) to (37), together with the equilibrium constants and Margules parameters derived from the ion-exchange experiments, values of M_A and M_B can be calculated if the value of TN is known or can be estimated by independent means. A value of TN is required as input into Equations (34), (36), and (37), and also in calculating the aqueous activity coefficient ratios, $(\gamma_A)^{z_B} / (\gamma_B)^{z_A}$. For a specific value of TN, a range of values corresponding to the activity coefficient ratios for solutions of almost pure A^{z_A+} to almost pure B^{z_B+} can be calculated. The aqueous activity coefficient ratios do not change very much for a particular TN. For example, for NaCl/CaCl₂ solutions at TN = 0.5 N, $(\gamma_{Na^+})^2 / (\gamma_{Ca^{2+}})$ changes by only ~6%, from 1.953 to 2.056, over a range of $M_{Na^+} / M_{Ca^{2+}}$ ratio from 0.498/0.001 to 0.002/0.249. The variation in activity coefficient ratios is smaller at lower total normalities or for solutions of homovalent cations (e.g. Na⁺/K⁺). For instance, for NaCl/CaCl₂ solutions at TN = 0.05 N, $(\gamma_{Na^+})^2 / (\gamma_{Ca^{2+}})$ changes by only ~0.3%, from 1.496 to 1.501, over a range of $M_{Na^+} / M_{Ca^{2+}}$ from 0.0498/0.0001 to 0.0002/0.0249. Likewise, for NaCl/KCl solutions at TN = 0.5 N, $\gamma_{Na^+} / \gamma_{K^+}$ changes by less than 3%, from 1.066 to 1.039, over a range of M_{Na^+} / M_{K^+} from 0.499/0.001 to 0.001/0.499. Therefore, although aqueous activity coefficient ratios are required to calculate solution compositions from zeolite data, for a given solution normality an activity coefficient ratio for a solution of median composition (e.g. equal normalities of A^{z_A+} and B^{z_B+}) can be used without resulting in a large error in predicted solution composition.

Groundwaters are typically dilute. For example, ionic strengths of Yucca Mountain saturated-zone groundwaters calculated by Turner et al. (1999), based on the comprehensive water chemistry data of Perfect et al. (1995), average about 0.019±0.099 M. Ionic strengths of porewaters from the hydrologically unsaturated zone of Yucca Mountain calculated from the data of Yang et al. (1996) average about 0.008±0.004 M. For these and other dilute groundwaters, it may be sufficient to use an activity coefficient ratio equal to one and obtain reasonable predictions of solution compositions.

Measured versus predicted solution compositions in binary systems. Pabalan and Bertetti (1999) equilibrated clinoptilolite powders with Na⁺/K⁺ and Na⁺/Ca²⁺ solutions and recovered the powders using standard filtration methods. The zeolites were contacted only with the solutions with which they equilibrated to avoid altering the clinoptilolite compositions during the filtration step. This method is particularly important for the Na⁺/Ca²⁺ system where, due to the concentration-valency effect, the zeolite composition may change significantly if the solid is contacted with deionized water (Stumm and Morgan 1996). Table 11 presents the chemical compositions of several clinoptilolite powders before and after equilibration with aqueous NaCl-KCl, NaCl-CaCl₂, NaNO₃-KNO₃, and NaNO₃-Ca(NO₃)₂ solutions at a total normality of 0.05 or 0.5 N. The zeolite compositions were determined by inductively coupled plasma emission spectrometry, subsequent to lithium metaborate fusion and dissolution in an HCl/HNO₃ matrix.

Table 11. Chemical composition of clinoptilolites before and after equilibration with (Na⁺ + K⁺) and (Na⁺ + Ca²⁺) solutions (from Pabalan and Bertetti, 1999).

Aqueous Mixtures	wt % SiO ₂	wt % TiO ₂	wt % Al ₂ O ₃	wt % Fe ₂ O ₃	wt % MgO	wt % Na ₂ O	wt % K ₂ O	wt % CaO	Total wt %
Na-form (unreacted)	68.28	0.04	11.28	0.40	0.16	6.36	0.66	0.02	87.20
0.5 N Na/K/Cl	67.81	0.06	11.17	0.36	0.17	1.91	7.52	0.00	89.00
	66.95	0.06	10.98	0.36	0.17	1.23	8.55	0.00	88.30
	65.82	0.06	10.75	0.35	0.16	0.55	9.29	0.01	86.99
	67.80	0.06	10.91	0.34	0.17	0.81	9.34	0.00	89.44
0.05 N Na/K/Cl	67.48	0.06	10.63	0.35	0.17	2.35	6.20	0.01	87.25
	67.58	0.04	10.55	0.25	0.25	0.55	8.43	0.00	87.65
	67.48	0.06	10.66	0.35	0.17	0.56	9.29	0.01	88.58
	67.34	0.06	10.58	0.35	0.17	0.32	9.64	0.00	88.46
0.05 N Na/K/NO ₃	68.00	0.06	10.78	0.35	0.17	4.83	2.66	0.00	86.85
	68.00	0.06	10.77	0.38	0.18	2.24	6.71	0.00	88.34
	67.30	0.06	10.79	0.35	0.17	1.52	7.59	0.00	87.78
	66.76	0.06	10.49	0.35	0.17	0.78	8.70	0.01	87.32
	65.65	0.06	10.46	0.34	0.16	0.46	8.85	0.01	85.99
	67.00	0.06	10.72	0.40	0.18	0.17	9.60	0.00	88.13
0.5 N Na/Ca/Cl	68.46	0.06	11.25	0.36	0.18	5.00	0.61	1.32	87.24
	67.02	0.06	10.95	0.4	0.19	4.43	0.62	1.79	85.46
	66.13	0.06	10.57	0.36	0.18	3.79	0.61	2.14	83.84
	67.17	0.06	10.73	0.36	0.19	3.03	0.63	3.10	85.27
	67.32	0.06	10.74	0.36	0.18	2.47	0.63	3.60	85.36
0.05 N Na/Ca/Cl	67.62	0.06	11.10	0.36	0.18	3.57	0.63	2.56	86.08
	67.54	0.05	11.00	0.36	0.20	2.55	0.58	3.52	85.80
	68.03	0.06	11.08	0.36	0.19	2.12	0.61	3.91	86.36
	68.62	0.06	11.33	0.36	0.19	1.72	0.62	4.36	87.26
	67.41	0.06	11.05	0.35	0.20	1.39	0.55	4.51	85.52
0.05 N Na/Ca/NO ₃	69.09	0.06	11.30	0.36	0.19	5.10	0.62	1.21	87.93
	66.08	0.06	10.89	0.35	0.18	3.28	0.60	2.66	84.10
	65.74	0.06	10.86	0.38	0.18	2.55	0.62	3.46	83.85
	66.17	0.06	10.98	0.37	0.19	1.90	0.60	4.13	84.40
	65.44	0.06	10.78	0.35	0.19	1.02	0.55	4.92	83.31

The measured Na_2O and K_2O weight percents given in Table 11 for the zeolites equilibrated with Na^+/K^+ solutions are listed in Table 12. These values were used to calculate \bar{X}_K and, from Equation (31), a_{Na}/a_K . The measured Na_2O and CaO weight percents given in Table 11 for the zeolites equilibrated with $\text{Na}^+/\text{Ca}^{2+}$ solutions are listed in Table 13 and were used to calculate \bar{X}_{Ca} and $(a_{\text{Na}})^2/a_{\text{Ca}}$. The \bar{X}_K values given in Table 12 were normalized to the molar amounts of Na^+ and K^+ only, whereas the \bar{X}_{Ca} values in Table 13 were normalized to the molar amounts of Na^+ and Ca^{2+} only. These calculations assumed that the small amounts of Ca^{2+} and Mg^{2+} present in the zeolite did not participate in the exchange process for the Na^+/K^+ system, and that K^+ and Mg^{2+} did not participate in the exchange for the $\text{Na}^+/\text{Ca}^{2+}$ mixture. This assumption is justified by the zeolite compositions given in Table 11 which show that, within analytical uncertainty, the MgO and CaO contents of the zeolites used in the Na^+/K^+ ion-exchange experiments remained equal to the MgO and CaO contents of the unreacted Na-clinoptilolite. Likewise, the K_2O and MgO contents of the zeolites from the $\text{Na}^+/\text{Ca}^{2+}$ experiments remained equal to those of the Na-clinoptilolite.

The composition of solutions in equilibrium with the zeolites were predicted from the values of a_{Na}/a_K and $(a_{\text{Na}})^2/a_{\text{Ca}}$ using Equations (34) to (37) and $\ln K_{(A,B)}$, W_A , and W_B given in Table 10. Aqueous activity coefficients required for the calculations were derived from the Pitzer equations and the parameters listed in Table 2. Values of $\gamma_{\text{Na}^+}/\gamma_{\text{K}^+} = 1.05$ and 1.007 and $(\gamma_{\text{Na}^+})^2/(\gamma_{\text{Ca}^{2+}}) = 1.98$ and 1.50 were used for 0.5 and 0.05 N NaCl/KCl solutions, respectively. Activity coefficient ratios of 1.019 and 1.49 were used for 0.05 N mixtures of $\text{NaNO}_3/\text{KNO}_3$ and $\text{NaNO}_3/\text{Ca}(\text{NO}_3)_2$, respectively. Table 12 compares the predicted aqueous concentrations of Na^+ and K^+ with values measured using ion-selective electrodes, and Table 13 compares predicted and measured Na^+ and Ca^{2+} solution concentrations. Measured and predicted concentrations are also compared in Figure 25.

The uncertainties in predicted Na^+ , K^+ , and Ca^{2+} solution concentrations were propagated assuming a $\pm 10\%$ error in the measured weight percents of Na_2O , K_2O , and CaO , but neglecting regression errors for $\ln K_{(A,B)}$, W_A , and W_B , and errors due to the use of a single value of activity coefficient ratio at a given solution normality. The results listed in Tables 12 and 13 and plotted in Figure 25 show that the predicted solution compositions agree very well with measured values, mostly within analytical uncertainty. This agreement demonstrates that it is possible to predict with confidence the cationic composition of an aqueous solution based on chemical analysis of zeolites with which it equilibrated, at least for simple two-cation systems for which the solution normality is known.

The solution concentration may be uncertain for natural aqueous systems. Therefore, it may not be possible to calculate accurate aqueous activity coefficients. In some cases, especially when solutions are dilute, it may be expeditious to use activity coefficient ratios equal to 1.0. For comparison, Tables 12 and 13 list K^+ , Ca^{2+} , and Na^+ concentrations calculated using activity coefficient ratios equal to 1.0. For aqueous solutions of K^+ and Na^+ , both monovalent cations, the solution compositions predicted using activity coefficient ratios equal to 1.0 do not differ much from the previously calculated values. On the other hand, for Ca^{2+} and Na^+ ion exchange, which involves heterovalent cations, the two sets of predicted compositions have significant differences, ranging from 4 to 26% at 0.05 N and from 7 to 38% at 0.5 N. However, considering the estimated error propagated from the uncertainties in zeolite composition, the values calculated using activity coefficient ratios equal to 1.0 are reasonable, especially in light of the fact that the differences between predicted and actual solution compositions become smaller at lower solution concentrations.

Table 12. Measured K^+ and Na^+ solution concentrations versus values predicted from measured clinoptilolite Na and K content. Also tabulated are cationic mole fractions of K^+ in the zeolite, \bar{X}_K , and predicted solution activity ratios of Na^+ and K^+ . Values in parentheses were derived using aqueous activity coefficient ratios equal to 1.0. From Pabalan and Bertetti (1999).

Aqueous Mixtures	wt % Na_2O	wt % K_2O	\bar{X}_K	a_{Na}/a_K	Calc. K^+ conc. (M)	Meas. K^+ conc. (M)	Calc. Na^+ conc. (M)	Meas. Na^+ conc. (M)
Na/K/Cl 0.5 N	1.91	7.52	0.721	5.906	0.076±0.019 (0.072)	0.061±0.002	0.424±0.019 (0.428)	0.444±0.009
	1.23	8.55	0.821	2.463	0.150±0.030 (0.144)	0.130±0.004	0.350±0.030 (0.356)	0.366±0.007
	0.55	9.29	0.917	0.7338	0.295±0.032 (0.288)	0.258±0.008	0.205±0.032 (0.212)	0.238±0.005
	0.81	9.34	0.884	1.207	0.233±0.034 (0.227)	0.209±0.006	0.267±0.034 (0.273)	0.298±0.006
Na/K/Cl 0.05 N	2.35	6.20	0.634	11.30	0.0041±0.0011 (0.0041)	0.0033±0.0001	0.0459±0.0011 (0.0459)	0.0465±0.0009
	0.55	8.43	0.910	0.8303	0.0274±0.0033 (0.0273)	0.0194±0.0006	0.0226±0.0033 (0.0227)	0.0306±0.0006
	0.56	9.29	0.916	0.7507	0.0287±0.0032 (0.0286)	0.0239±0.0007	0.0213±0.0032 (0.0214)	0.0271±0.0005
	0.32	9.64	0.952	0.3646	0.0367±0.0024 (0.0366)	0.0327±0.0010	0.0133±0.0024 (0.0134)	0.0174±0.0003
Na/K/ NO_3 0.05 N	4.83	2.66	0.266	125.1	0.0004±0.0001	0.0003±0.00001	0.0496±0.0001	0.0476±0.0010
	2.24	6.71	0.663	9.181	0.0050±0.0013	0.0034±0.0001	0.0451±0.0013	0.0457±0.0009
	1.52	7.59	0.767	4.063	0.0100±0.0023	0.0069±0.0002	0.0401±0.0023	0.0404±0.0008
	0.78	8.70	0.880	1.262	0.0223±0.0033	0.0154±0.0005	0.0278±0.0033	0.0314±0.0006
	0.46	8.85	0.927	0.6237	0.0310±0.0031	0.0248±0.0007	0.0191 ±0.0031	0.0243±0.0005
	0.17	9.60	0.974	0.1799	0.0425±0.0015	0.0368±0.0011	0.0076 ±0.0015	0.0121±0.0002

Table 13. Measured Ca^{2+} and Na^+ solution concentrations versus values predicted from measured clinoptilolite Na and Ca content. Also tabulated are cationic mole fractions of Ca^{2+} in the zeolite, \bar{X}_{Ca} , and predicted solution activity ratios of Na^+ and Ca^{2+} . Values in parentheses were derived using aqueous activity coefficient ratios equal to 1.0. From Pabalan and Bertetti (1999).

Aqueous Mixtures	wt % Na_2O	wt % CaO	\bar{X}_{Ca}	$(a_{\text{Na}})^2/(a_{\text{Ca}})$	Calc. Ca^{2+} conc. (M)	Meas. Ca^{2+} conc. (M)	Calc. Na^+ conc. (M)	Meas. Na^+ conc. (M)
Na/Ca/Cl 0.5 N	5.0	1.32	0.127	5.868	0.052±0.012 (0.032)	0.051±0.002	0.395±0.025 (0.435)	0.409±0.008
	4.43	1.79	0.183	2.314	0.089±0.019 (0.061)	0.085±0.003	0.323±0.037 (0.377)	0.345±0.007
	3.79	2.14	0.238	1.005	0.124±0.022 (0.095)	0.118±0.005	0.252±0.043 (0.309)	0.260±0.005
	3.03	3.1	0.361	0.1885	0.184±0.018 (0.162)	0.180±0.007	0.133±0.036 (0.175)	0.155±0.003
	2.47	3.6	0.446	0.06527	0.208±0.013 (0.194)	0.199±0.008	0.083±0.026 (0.112)	0.100±0.002
	3.57	2.56	0.284	0.5259	0.0047±0.0016 (0.0035)	0.0039±0.0002	0.0406±0.0031 (0.0430)	0.0406±0.0008
Na/Ca/Cl 0.05 N	2.55	3.52	0.433	0.07686	0.0124±0.0026 (0.0107)	0.0105±0.0004	0.0252±0.0052 (0.0286)	0.0285±0.0006
	2.12	3.91	0.505	0.03232	0.0158±0.0023 (0.0143)	0.0136±0.0005	0.0184±0.0046 (0.0215)	0.0214±0.0004
	1.72	4.36	0.583	0.01291	0.0187±0.0018 (0.0175)	0.0173±0.0007	0.0126±0.0035 (0.0150)	0.0159±0.0003
	1.39	4.51	0.642	0.00658	0.0203±0.0013 (0.0194)	0.0194±0.0008	0.0094±0.0026 (0.0113)	0.0124±0.0002
	5.1	1.21	0.116	7.251	0.0005±0.0002	0.0005±0.00002	0.0490±0.0003	0.0496±0.0010
	3.28	2.66	0.309	0.3714	0.0059±0.0019	0.0051±0.0002	0.0382±0.0037	0.0392±0.0008
Na/Ca/ NO_3 0.05 N	2.55	3.46	0.429	0.0809	0.0122±0.0026	0.0101±0.0004	0.0257±0.0051	0.0303±0.0006
	1.9	4.13	0.546	0.01999	0.0174±0.0020	0.0159±0.0006	0.0153±0.0040	0.0177±0.0004
	1.02	4.92	0.727	0.00243	0.0220±0.0008	0.0217±0.0009	0.0060±0.0015	0.0069±0.0001

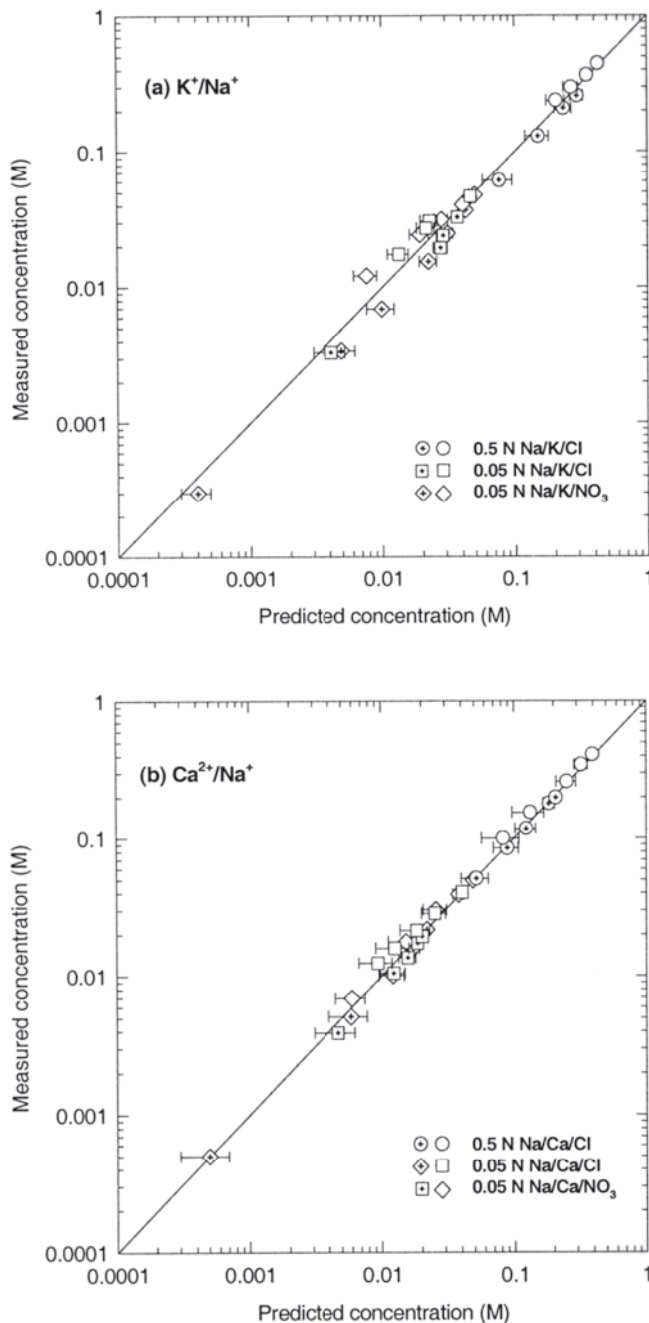


Figure 25. Comparison of measured Na^+ , K^+ , and Ca^{2+} concentrations in the aqueous phase with values calculated based on the composition of the coexisting zeolite phase. Open symbols are values for Na^+ concentrations. Cross-hair symbols in (a,b) are values for K^+ or Ca^{2+} concentrations. From Pabalan and Bertetti (1999).

ANION EXCHANGE ON SURFACTANT-MODIFIED ZEOLITES

The net negative structural charge of zeolites that results in the favorable ion-exchange selectivity for many cations also causes natural zeolites to have little or no affinity for anions, such as the oxyanions of toxic metals like chromate (CrO_4^{2-}), selenate (SeO_4^{2-}), and pertechnetate (TcO_4^-). Likewise, sorption affinity for actinides such as uranium and neptunium, which sorb primarily through a surface complexation mechanism, is also limited (Pabalan et al. 1998; Bertetti et al. 1998).

Cationic surfactants have been used to modify zeolite surfaces in attempts to enhance the sorptive capabilities of natural zeolites. Cationic surfactants in the aqueous phase associate in micelles due to a hydrophobic effect. In the presence of zeolites, the

surfactant sorbs to the negatively charged zeolite surface and forms a bilayer of surfactant molecules similar to a lipid layer (Li and Bowman 1997; Sullivan et al. 1998). Surfactant sorption causes the surface charge to change from negative to positive and the organic carbon content of the zeolite to increase to about 5 wt %. The positive surface charge, which provides sites for sorption of anions, results when positively charged surfactant head groups are presented to the surrounding solution, where they are balanced by counterions that can be replaced by other anions in solution (Li and Bowman 1997; Sullivan et al. 1998). The relatively large surfactant molecules do not enter the zeolite channels or access internal cation-exchange sites. Therefore, some of the original CEC of the zeolite is retained for sorbing cations. In addition, the organic-rich surface layer provides a partitioning medium for sorption of nonpolar organics, such as chlorinated solvents and fuel components. Therefore, the surfactant-modified zeolite (SMZ) can simultaneously sorb inorganic cations, inorganic anions, and nonpolar organics (Haggerty and Bowman 1994; Bowman et al. 1995). The magnitude and stability of sorption of the surfactant on the zeolite and of anion exchange are influenced by the counterion (e.g. Cl^- , Br^- , or HSO_4^-) of the surfactant (Li and Bowman 1997).

Recent studies have shown that treatment of clinoptilolite with cationic surfactants, e.g. hexadecyltrimethylammonium-bromide (HDTMA), yields an SMZ that has a strong affinity for selenate and chromate, as well as nonpolar organics, such as benzene, 1,1,1-trichloroethane, and perchloroethylene, but that also has cation-exchange selectivity for heavy-metal cations, such as Pb^{2+} (Haggerty and Bowman 1994; Bowman et al. 1995). Additional studies investigating actinide sorption on SMZs indicate that surfactant modification also enhances the ability of clinoptilolite to sorb U^{6+} , particularly at pHs greater than 6 where U^{6+} sorption on unmodified zeolite is typically low due to formation of anionic U^{6+} aqueous carbonate complexes (Prikryl and Pabalan 1999). The enhanced sorption of U^{6+} is interpreted to be due to anion exchange with counterions on the external portion of a surfactant bilayer or admicelles (Prikryl and Pabalan 1999).

Although data on anion exchange on SMZs are limited compared with the data available on cation exchange on natural zeolites, published studies suggest that surfactant modification offers the potential to further enhance the industrial and environmental applications of natural zeolites.

RECOMMENDATIONS FOR FUTURE WORK

Although numerous studies have been conducted on ion-exchange equilibria involving natural zeolites, a systematic and comprehensive evaluation of ion-exchange data from different sources is not available. As shown by the tabulated values in this chapter, there are significant differences in the ion-exchange equilibrium constants and Gibbs free energies reported by different investigators for the same types of natural zeolites at the same temperatures. These differences could be due to the variability in composition and purity of mineral samples used in the experiments, but they also could be a result of the different approaches used in interpreting the ion-exchange data. An attempt was made in this chapter to evaluate literature data on clinoptilolite ion exchange and to provide a set of self-consistent thermodynamic parameters based on a specific approach for calculating solid solution and aqueous phase activity coefficients. The evaluation, however, is not comprehensive, and it would be useful to derive thermodynamic parameters for other binary systems and other zeolite minerals for which experimental data are available. Moreover, although multiple studies have been published for some binary cation mixtures (e.g. ion exchange between clinoptilolite and Cs^+/Na^+ , $\text{NH}_4^+/\text{Na}^+$, $\text{Ca}^{2+}/\text{Na}^+$, and K^+/Na^+ solutions), data on other binary systems (e.g. mixtures with Mg^{2+} and Ba^{2+}) are not available. For some of these poorly understood binary

systems, ion-exchange equilibrium constants and Gibbs free energies may be derived using the triangle rule. However, experimental data at one solution normality would still be required to constrain the shape of the isotherm. For binary systems with insufficient data to apply the triangle rule, it may be useful to evaluate the utility of correlation methods for predicting ion-exchange thermodynamic parameters.

Most published ion-exchange data on natural zeolites involve the exchange of two cations only. Little attention has been paid to the problem of understanding multicomponent ion-exchange equilibria, despite the fact that ion-exchange processes in natural systems generally involve more than two ions. Multicomponent ion-exchange studies are challenging. A large amount of experimental data is needed to completely characterize a ternary system and numerical analysis of the data is difficult. For a system with more than three ions, Grant and Fletcher (1993) concluded that the amount of data required to characterize the system is almost prohibitive. Nevertheless, experimental data on ternary and more complex mixtures are needed if progress is to be made in developing and evaluating thermodynamic models that can be used to predict ion-exchange equilibria in natural systems. Thermodynamic modeling of multicomponent ion-exchange equilibria is computationally more complex, but the basic principles are the same as those for binary exchange reactions. In particular, it would be useful to test the ability of the Wilson model, which does not require parameters beyond the binary terms, to predict ion-exchange equilibria in ternary and more complex mixtures.

Finally, several studies report ion-exchange data and thermodynamic parameters at temperatures other than 298 K. Some of the reported values are listed in the tables in this chapter. The temperature dependence of ion-exchange equilibria was not addressed in this chapter and a critical review of literature information on the enthalpies of ion-exchange reactions would be useful.

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APPENDIX

Equations for calculating \bar{E}_A , E_A , $K_{v(A,B)}$, and associated uncertainties from experimental data

Values of \bar{E}_A and E_A can be calculated from the measured zeolite mass (W , grams), solution volume (V , liters), cation-exchange capacity (CEC, milliequivalents per gram), and initial (i) and final (f) molar concentrations (M , moles/liter solution) of A^{z_A+} and B^{z_B+} using the equation

$$\bar{E}_A = \frac{z_A(M_{A,i} - M_{A,f})V}{W \cdot \text{CEC}}; \quad E_A = \frac{z_A M_{A,f}}{\text{TN}} \quad (\text{A-1})$$

where TN is the total cation normality (equivalents per liter) of the aqueous phase. If measured concentrations of the competing cation B^{z_B+} are available, values of \bar{E}_A and E_A can be independently calculated from the equation

$$\bar{E}_A = \frac{z_B(M_{B,f} - M_{B,i})V}{W \cdot \text{CEC}}; \quad E_A = 1 - \frac{z_B M_{B,f}}{\text{TN}} \quad (\text{A-2})$$

In a similar manner, one set of $\ln K_{v(A,B)}$ values can be calculated from the A^{z_A+} analytical data and another set from the B^{z_B+} data using the respective equations

$$K_{v(A,B)} = \frac{(\bar{X}_A)^{z_B} [(TN - z_A M_A)/z_B]^{z_A}}{(1 - \bar{X}_A)^{z_A} (M_A)^{z_B}} \cdot \frac{(\gamma_B)^{z_A}}{(\gamma_A)^{z_B}} \quad (\text{A-3})$$

and

$$K_{v(A,B)} = \frac{(1 - \bar{X}_B)^{z_B} (M_B)^{z_A}}{(\bar{X}_B)^{z_A} [(TN - z_B M_B)/z_A]^{z_B}} \cdot \frac{(\gamma_B)^{z_A}}{(\gamma_A)^{z_B}} \quad (\text{A-4})$$

From Pabalan (1994), the uncertainties in \bar{E}_A and E_A calculated from the A^{z_A+} data (Eqn. A-1) are given by

$$\left(\frac{U_{\bar{E}_A}}{\bar{E}_A}\right)^2 = \left(\frac{U_{M_{A,i}}}{M_{A,i} - M_{A,f}}\right)^2 + \left(\frac{U_{M_{A,f}}}{M_{A,i} - M_{A,f}}\right)^2 + \left(\frac{U_V}{V}\right)^2 + \left(\frac{U_W}{W}\right)^2 + \left(\frac{U_{\text{CEC}}}{\text{CEC}}\right)^2 \quad (\text{A-5})$$

and

$$\left(\frac{U_{E_A}}{E_A}\right)^2 = \left(\frac{U_{M_{A,f}}}{M_{A,f}}\right)^2 + \left(\frac{U_{TN}}{TN}\right)^2. \quad (\text{A-6})$$

The equation for the uncertainties in \bar{E}_A calculated from the B^{z_B+} data (Eqn. A-2) is the same as Equation (A-5), except the molarities are those for B^{z_B+} . The uncertainty equation for E_A calculated from B^{z_B+} data is slightly different from Equation (A-6), and is given by

$$\left(\frac{U_{E_A}}{E_A}\right)^2 = \left(\frac{z_B M_{B,f}}{TN - z_B M_{B,f}}\right)^2 \cdot \left[\left(\frac{U_{M_{B,f}}}{M_{B,f}}\right)^2 + \left(\frac{U_{TN}}{TN}\right)^2 \right]. \quad (\text{A-7})$$

Note that Equation (A-5) has terms with concentration differences in the denominator. Where the difference in initial and final concentration is small, the uncertainty in the calculated parameter can be large. Therefore, errors in \bar{E}_A calculated from the A^{z_A+} analysis become large as \bar{E}_A approaches one. On the other hand, errors in \bar{E}_A calculated from the B^{z_B+} data become large as \bar{E}_A approaches zero. These trends explain why it is important to analyze the solution concentrations of both cations participating in the exchange reaction when constructing ion-exchange isotherms. In this manner, the ion-exchange isotherm is well-constrained throughout the entire composition range

Uncertainties in the selectivity coefficient, $K_{v(A,B)}$, derived using A^{z_A+} analytical data (Eqn. A-3) can be calculated from

$$\left(\frac{U_{K_v}}{K_v}\right)^2 = \left(\frac{z_A U_{\bar{X}_A} + z_B U_{\bar{X}_A}}{1 - \bar{X}_A + \bar{X}_A}\right)^2 + \left(\frac{z_A^2 U_{M_A} + z_B U_{M_A}}{TN - z_A M_A + M_A}\right)^2 + \left(\frac{z_A U_{\gamma_B}}{\gamma_B}\right)^2 + \left(\frac{z_B U_{\gamma_A}}{\gamma_A}\right)^2. \quad (\text{A-8})$$

The corresponding uncertainty equation for $K_{v(A,B)}$ calculated from the B^{z_B+} data (Eqn. A-4) can be derived by interchanging coefficients A and B in Equation (A-8). Also,

$$U_{\ln K_{v(A,B)}} = \frac{U_{K_{v(A,B)}}}{K_{v(A,B)}} \quad (\text{A-9})$$

and

$$\frac{U_{\bar{X}_A}}{\bar{X}_A} = \frac{(z_A - z_B)U_{\bar{E}_A}}{z_A + (z_B - z_A)\bar{E}_A} + \frac{U_{\bar{E}_A}}{\bar{E}_A}. \quad (\text{A-10})$$