

Particle Distribution in a Microporous Material

Andreas Kunzmann, Roland Seifert, and Gion Calzaferri*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

Received: June 24, 1998; In Final Form: November 3, 1998

Equilibria in zeolites and other microporous materials are discussed. We present an *independent particles in a box* approach, which leads to a thermodynamic description of internal occupation equilibria of the type $ZX_{i-1} + ZX_{i+1} \rightleftharpoons 2ZX_i$, where Z denotes the framework of the material and X the particles that can interchange places. The independent particles in a box are defined by considering a crystal consisting of a finite number of unit cells or boxes each of which can be filled with a specific number of particles. All empty sites in a box have equal probability to be occupied, independent of the number of particles present, as long as sites are available. Each time a particle does fall in a box, the probability for a next one to hit this box is reduced by 1 divided by the number of sites available in an empty box. Hence, as soon as a box is filled, the probability for a particle to hit it becomes zero. The maximum number of particles in the system is equal to the maximum number of sites in a box multiplied by the number of boxes. This allows equilibrium constants and the decrease of entropy as a function of the equivalent fraction of exchanging species to be calculated. We show that the plot of the logarithm of the equilibrium constant versus the equivalent fraction of exchanging species is not linear and that the nonlinearity is caused by the decrease of entropy. On the basis of this observation, we suggest the independent particles in a box to be used as a reference for “ideal behavior” and to serve as a reference for determining activity coefficients. The generalization of the theory leads to the independent particles in boxes with different sites. It is discussed in detail with regard to two nonequivalent sites corresponding to the internal equilibria $ZX1_{\rho1}X2_{\rho2} \rightleftharpoons ZX1_{\rho+1}X2_{\rho2-1}$ in which X1 and X2 are the same species but occupy site 1 and 2, respectively, of a box. We show the solution of this problem and explain the distribution of the particles among the different sites as a function of the average exchange degree.

Introduction

Ion exchange equilibria and the distribution of ions, atoms, or molecules in zeolites and in other microporous materials have been investigated both by means of experimental and theoretical methods, some aspects of which are well understood; see, e.g., refs 1–15. However, the handling of many relevant cases remains unsatisfactory, and it is desirable to develop a well-defined and simple system that can be used as an “ideal case reference system”. We found that the independent particles in a box can be used for this purpose. Its consequences have not been explored so far. We do it now because this well-defined system leads to considerable insight and improves our understanding of microporous material. We consider a crystal consisting of a finite number of unit cells or boxes each of which can be filled with a specific number of particles. All empty sites in a box have equal probability to be occupied, independent of the number of particles present, as long as sites are available. Each time a particle does fall in a box, the probability for a next one to hit this box is reduced by 1 divided by the number of sites available in an empty box. Hence, as soon as a box is filled, the probability for a particle to hit it becomes zero. The maximum number of particles in the system is equal to the maximum number of sites in a box multiplied by the number of boxes. In a zeolite, this corresponds to the situation in which no coordination site is occupied with preference. An example for which this description provides a good understanding is a zeolite A in which some of the Na^+ have been exchanged by

* Corresponding author. Phone: +41 31 631 4226. E-mail: calza@solar.iac.unibe.ch.

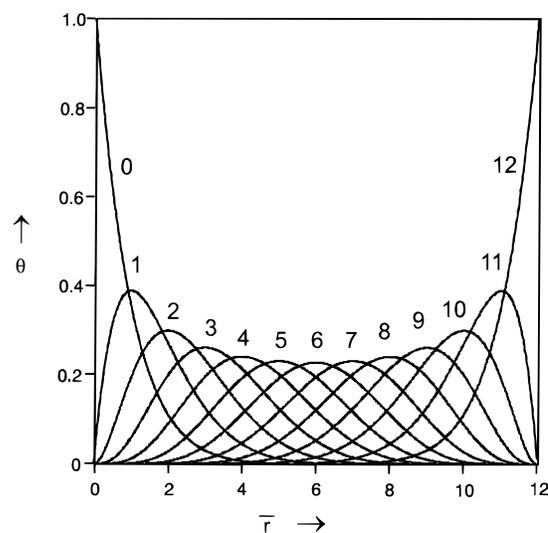
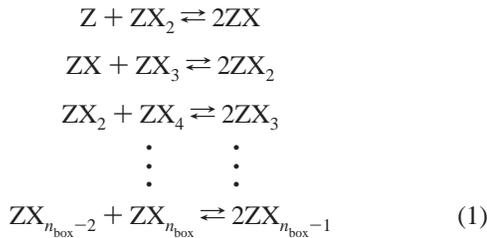


Figure 1. Particle distribution θ of a system consisting of equivalent boxes, each of which contains 12 equivalent sites, as a function of the average number of particles in a box \bar{r} . The line marked as 0 indicates the relative number of empty boxes; 1 indicates the relative number of boxes containing one particle and so on.

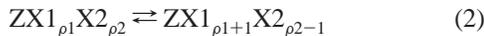
another monovalent cation M^+ such as K^+ , Ag^+ , or others, leading to $\text{Na}^+_{12-x}\text{M}^+_x[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]$ despite the fact that site preferences have been reported.^{16–18} We have recently used it to study the dependency of the electronic spectra of activated $\text{Ag}^+_{12-x}\text{M}^+_x[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]$ on the exchange degree x .¹⁹ Figure 1 illustrates the calculated statistical distribution of silver ions in the unit cells as a function of the average exchange degree \bar{r} ,

which is equal to x . The distribution shows, e.g., that the share of unit cells with one Ag^+ increases until an average content of one Ag^+ per unit cell is reached. With an average exchange degree as low as 1.5 Ag^+ per unit cell, the share of cells with only one Ag^+ is substantially smaller already and roughly corresponds to the sum of the shares with more than one Ag^+ .

In the present work, we first explain the independent particles in a box case. We show that the results lead to a thermodynamic description of the internal occupation equilibrium 1, for which the equilibrium constants and the change of entropy are calculated.



We compare the results with the so-called Kielland plot,¹ which has been generally accepted to be useful for discussing activities in ion exchange equilibria in zeolites, clay minerals, and other materials; see, e.g., refs 2–6. We propose to substitute the Kielland plot by the independent particles in a box equation as a reference for ideal behavior. We then introduce the generalization of the theory for boxes with unequal sites and we illustrate how the fast increasing complexity of the system can be handled for boxes with two different sites, corresponding to the internal equilibrium 2 in which X1 and X2 are the same species but coordinated to the sites 1 and 2, respectively.



Independent Particles in Boxes

We describe microcrystals, each consisting of N_{uc} unit cells or boxes, each of which can be filled with up to n_{box} particles. All empty sites in a box have equal probability to be occupied, independent of the number n of particles present. Its maximum number n_{max} in a crystal is given by

$$n_{\text{max}} = n_{\text{box}}N_{\text{uc}} \quad (3)$$

Each time a particle falls in a box the probability for a next one to hit that box reduces by $1/n_{\text{box}}$; hence, once a box is filled, the probability for a next particle to hit it becomes zero. This is how we define the independent particles in a box. The reduced number $\theta(r)$ of particles in the system is defined as

$$\theta_i(r) = \frac{N_{r,i}}{N_{\text{uc}}} \quad (4)$$

where $N_{r,i}$ is the number of boxes containing r particles in a crystal filled with i of them. We assume that a total of n particles are already present in our sample and that we add an additional number Δn of them in a try i . This means that the number of empty boxes $N_{0,i-1}$ reduces to $N_{0,i}$ and the number of boxes containing r particles $N_{r,i-1}$ changes to $N_{r,i}$

$$N_{0,i} = N_{0,i-1} - p_0 \Delta n N_{0,i-1} \quad (5)$$

$$N_{r,i} = N_{r,i-1} + p_{r-1} \Delta n N_{r-1,i-1} - (p_r \Delta n) N_{r,i-1} \quad (6)$$

In these equations $p_r \Delta n$ is the probability that boxes containing r particles vanish by receiving an additional number of

particles Δn and $p_{r-1} \Delta n$ is the probability that boxes containing $r-1$ particles are transformed into boxes containing r of them. If $\Delta n = 1$ particles are added to the sample, this can be expressed as follows:

$$p_r \times 1 = (n_{\text{box}} - r) \frac{1}{n_{\text{box}} N_{\text{uc}} - n} \quad (7)$$

or

$$p_r = \frac{n_{\text{box}} - r}{n_{\text{box}} N_{\text{uc}} - n} \quad \text{for } n < n_{\text{box}} N_{\text{uc}} \quad \text{and } n_{\text{box}} \geq r \geq 1 \quad (8)$$

Using $\Delta N_r = N_{r,i} - N_{r,i-1}$, eqs 4 and 5 become after some rearrangement:

$$\frac{\Delta N_0}{\Delta n} = -p_0 N_0 \quad (9)$$

$$\frac{\Delta N_r}{\Delta n} = p_{r-1} N_{r-1} - p_r N_r \quad \text{for } n_{\text{box}} \geq r \geq 1 \quad (10)$$

We express the initial conditions, when all boxes are empty, as a function of the number of particles n , the number of positions in a box n_{box} , and the number of boxes N_{uc} .

$$N_0(0, n_{\text{box}}, N_{\text{uc}}) = N_{\text{uc}} \quad (11)$$

$$N_r(0, n_{\text{box}}, N_{\text{uc}}) = 0 \quad \text{for } n_{\text{box}} \geq r \geq 1 \quad (12)$$

With these initial conditions, the eqs 9 and 10 can be solved explicitly. The solution is given in eq 13. Its derivation is given in the appendix.

$$\begin{aligned} N_r(n, n_{\text{box}}, N_{\text{uc}}) = & \\ & \frac{n_{\text{box}}!}{(n_{\text{box}} - r)! r!} \frac{N_{\text{uc}}}{(n_{\text{box}} N_{\text{uc}})^{n_{\text{box}}}} n^r (n_{\text{box}} N_{\text{uc}} - n)^{n_{\text{box}} - r}, \\ & r = 0, 1, \dots, n_{\text{box}} \end{aligned} \quad (13)$$

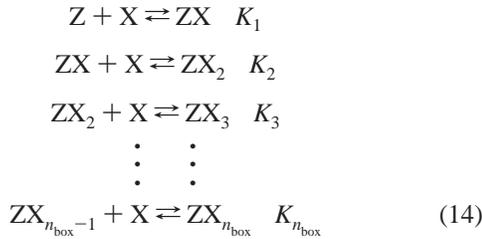
This ends the mathematical part of the independent particle case. Before exploring its meaning, we should add that eq 13 differs from the hypergeometric distribution²⁰ significantly in that it allows us to calculate equilibrium constants directly while the hypergeometric distribution does not.

We first investigate a porous nanocrystal consisting of a certain number of equivalent boxes each of which bears $n_{\text{box}} = 12$ equivalent places. We would like to know the distribution of the particles among the boxes when filling the nanocrystal by throwing in one particle after the other. Figure 1 shows the relative number of boxes containing 0, 1, 2, ..., 12 particles, which is the particle distribution θ , as a function of the reduced particle number $\bar{r} = n/N_{\text{uc}}$. The reduced particle number \bar{r} corresponds to the average number of particles in a box. An example for which these results provide a good understanding of experimental observations is a zeolite A in which some of the sodium cations have been exchanged by another monovalent cation M^+ such as K^+ , Ag^+ , or others, leading to $\text{Na}^+_{12-x} \text{M}^+_x [\text{Al}_{12} \text{Si}_{12} \text{O}_{48}]$. It has recently been used by us to study the dependency of the electronic spectra of activated silver-containing zeolite A on the exchange degree x .¹⁹ In this study, each pseudo-unit cell was identified as a box with $n_{\text{box}} = 12$ equivalent sites. The size of the individual zeolite crystals was not important because

TABLE 1: Equilibrium Constants K_r Calculated from Eq 23 and Entropy Change in J/(K mol)

| r | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|--------------|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------------------|
| K_r | 1.0 | 0.458 | 0.278 | 0.178 | 0.133 | 0.097 | 0.071 | 0.052 | 0.037 | 0.025 | 0.015 | 6.94×10^{-3} |
| ΔS_r | 0.0 | -6.49 | -10.6 | -13.9 | -16.8 | -19.4 | -21.9 | -24.6 | -27.4 | -30.7 | -34.8 | -41.3 |

all boxes were assumed to be equal. The results shown in Figure 1 can therefore be interpreted as distribution of the Ag^+ ions in the zeolite A as a function of the exchange degree x , which takes the same values as \bar{r} . We now investigate the thermodynamic equilibrium of a system consisting of $n_{\text{box}} + 1$ species ZX_ρ , $\rho = 0, 1, 2, \dots, n_{\text{box}}$.



The equilibrium constants K_r are given by

$$K_r = \frac{[\text{ZX}_r]}{[\text{X}][\text{ZX}_{r-1}]}, \quad r = 1, 2, \dots, n_{\text{box}} \quad (15)$$

The concentrations of the individual species $[\text{ZX}_\rho]$ as a function of the concentration of free X can be expressed as follows:²¹

$$[\text{ZX}_\rho] = \frac{[\text{X}]^\rho \prod_{j=0}^{\rho} K_j}{\sum_{i=0}^{n_{\text{box}}} [[\text{X}]^i \prod_{j=0}^i K_j]} A_0 \quad (16)$$

where K_0 is equal to 1 by definition and A_0 is the total concentration of the ZX_ρ species.

$$A_0 = \sum_{\rho=0}^{n_{\text{box}}} [\text{ZX}_\rho] \quad (17)$$

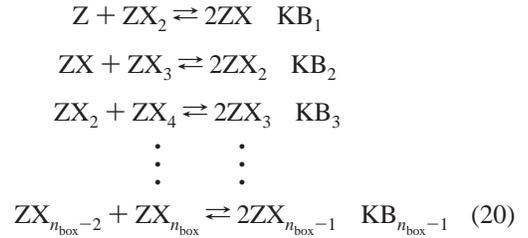
The total concentration of bound X species can be expressed as

$$[\text{X}]_{\text{tot}} = \sum_{\rho=0}^{n_{\text{box}}} \rho [\text{ZX}_\rho] \quad (18)$$

The equilibrium 14 can be compared with the independent particles in a box if we use the ratio between the two equilibrium constants, e.g., K_r and K_{r+1} , which we abbreviate as KB_r .

$$\text{KB}_r = \frac{K_r}{K_{r+1}} = \frac{[\text{ZX}_r]^2}{[\text{ZX}_{r-1}][\text{ZX}_{r+1}]}, \quad r = 1, 2, \dots, n_{\text{box}} - 1 \quad (19)$$

This describes the following equilibria that correspond to the ‘internal occupation equilibrium’ of the material.



The equilibrium constants KB_r can be calculated because the number of boxes containing r particles are directly proportional to the concentration of the ZX_ρ species. Thus we obtain

$$\text{KB}_r = \frac{[N_r(n, n_{\text{box}}, N_{\text{uc}})]^2}{[N_{r+1}(n, n_{\text{box}}, N_{\text{uc}})][N_{r-1}(n, n_{\text{box}}, N_{\text{uc}})]} \quad (21)$$

Inserting the solution for $N_r(n, n_{\text{box}}, N_{\text{uc}})$ given in eq 13 leads after some rearrangement to the following astonishingly simple result:

$$\text{KB}_r = \frac{r+1}{r} \left(\frac{n_{\text{box}} - r + 1}{n_{\text{box}} - r} \right) \quad (22)$$

and therefore to

$$K_{r+1} = K_r \left[\frac{r+1}{r} \left(\frac{n_{\text{box}} - r + 1}{n_{\text{box}} - r} \right) \right]^{-1} \quad (23)$$

From eq 16 it is obvious that multiplying each K_r by the same constant does not affect the concentrations $[\text{ZX}_\rho]$ of the individual species. We can therefore choose $K_1 = 1$ without loss of generality. This means that not only the equilibrium constants KB_r can be calculated from the solution of the independent particles in a box but, more importantly, also K_r . Using eqs 16–18 and 23 it is possible to calculate the concentrations $[\text{ZX}_\rho]$. We illustrate this for $n_{\text{box}} = 12$ in Table 1, where the equilibrium constants and the entropy change calculated from eqs 23 and 25 are reported, and in Figure 2, where we show the concentrations of the individual species ZX_ρ as a function of the free X concentration, normalized by the maximum of $[\text{X}]_{\text{tot}}$. The progress of the concentrations of the ZX_ρ species with large ρ illustrates the constraints imposed on the system by the decreasing entropy with increasing ρ . Since there is no enthalpy change involved, the change of the entropy ΔS_r can be expressed by eq 25.

$$\Delta G_r = -RT \log K_r \quad (24)$$

$$\Delta S_r = R \log K_r \quad (25)$$

We now compare the results with selectivity constants as used, for example, for describing zeolite ion exchange equilibria.⁶ We investigate monovalent ions and activity coefficients of one, because only this case can be directly compared with the independent particles in a box.

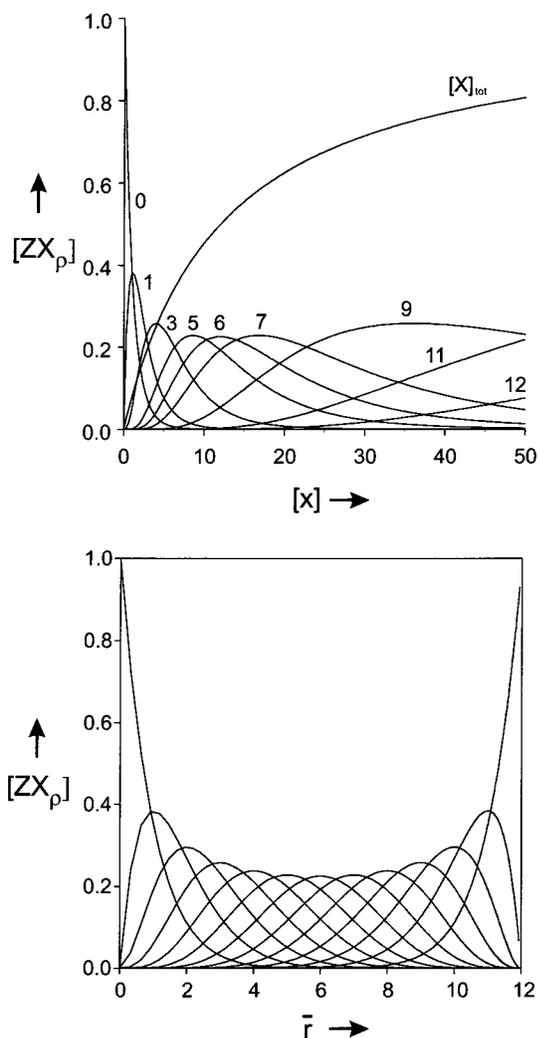
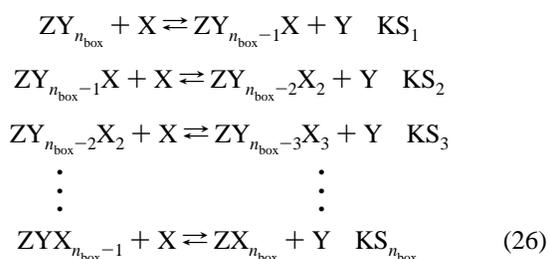


Figure 2. Illustration of the equilibrium 14 for a system consisting of 13 species ZX_ρ , $\rho = 0, 1, 2, \dots, 12$. (top) Relative concentrations of the ZX_ρ species and total concentration $[X]_{tot}$ of bound X species, normalized by the maximum of $[X]_{tot}$, versus the concentration of free X. (bottom) Relative concentrations of the ZX_ρ species ($\rho = 0, 1, \dots, 12$) versus the average number of particles in a box \bar{r} .



The selectivity constants KS_r are defined as follows:

$$KS_r = \frac{[ZY_{n_{box}-r}X_r][Y]}{[ZY_{n_{box}-(r-1)}X_{r-1}][X]}, \quad r = 1, 2, \dots, n_{box} \quad (27)$$

It is easy to see that the ratio between two of these selectivity constants can be identified with the equilibrium constants KB_r , similar to the case in in eq 19.

$$\frac{KS_r}{KS_{r+1}} = \frac{[ZY_{n_{box}-r}X_r]^2}{[ZY_{n_{box}-(r-1)}X_{r-1}][ZY_{n_{box}-(r+1)}X_{r+1}]} \quad (28)$$

This means that we can also calculate the selectivity constants for monovalent ion exchange of a zeolite.

$$KS_{r+1} = KS_r \left[\frac{r+1}{r} \left(\frac{n_{box}-r+1}{n_{box}-r} \right) \right]^{-1} \quad (29)$$

This corresponds to eq 23, which means that all consequences derived from it also apply to the ion exchange equilibrium 26. Zeolite ion exchange equilibria have often been inspected by means of the so-called Kielland plot.¹ The reasoning of Jacob Kielland was that the influence of the activity coefficients γ_{ZM} and γ_{ZN} in equilibria of the following type



can be taken into account by a linear relation:

$$\log K_a = \log \frac{a_{Zn}a_{M}}{a_{ZM}a_{N}} = \log \frac{[N]_Z a_M}{[M]_Z a_N} + C([M]_Z - [N]_Z) \quad (31)$$

where a_{ZN} , a_{ZM} , a_N and a_M are the activities of the corresponding species. $[M]_Z$ and $[N]_Z$ are the concentrations of M and N in the zeolite Z, and C is an empirical constant. This equation has been later used in the following form:^{4,6}

$$\log K'_a = \log K_a + b\Theta_Z \quad (32)$$

where b is an empirical constant, K'_a is the corrected selectivity constant, and Θ_Z is the equivalent fraction of exchanging species

$$K'_a = \frac{[N]_Z a_M}{[M]_Z a_N} \quad (33)$$

$$\Theta_Z = \frac{[N]_Z}{[N]_Z + [M]_Z} \quad (34)$$

In the systems discussed in this work, the sum $[N]_Z + [M]_Z$ is a constant and Θ_Z is therefore equal to the exchange degree x , which is always defined in an analogous manner as we explained for the example $Na^+_{12-x}M^+_x[Al_{12}Si_{12}O_{48}]$, divided by the maximum number of places per unit cell n_{box} .

$$\Theta_Z = \frac{x}{n_{box}}, \quad 0 \leq \Theta_Z \leq 1 \quad (35)$$

We thus write the Kielland equation for the equilibrium 26 as follows:

$$\log KS = a + b\Theta_Z \quad (36)$$

where a and b are empirical parameters. The equivalent to the Kielland plot of the independent particles in a box has the following form:

$$\log KS_{r+1} = \log KS_r - \log \left[\frac{r+1}{r} \left(\frac{n_{box}-r+1}{n_{box}-r} \right) \right] \quad (37)$$

The derivative of KS_{r+1} with respect to r is obviously not a constant, which means that the equivalent 37 to the Kielland plot is not linear. In Figure 3, we illustrate how $\log KS_{r+1}$ changes as a function of r and we compare this with the linear function 36 for which the parameters a and b have been adjusted to fit eq 37 as well as possible. We see that the deviation from linearity of 37 is small, in the range between $0.1 < \Theta_Z < 0.9$, where the best experimental data are available. Since the activity

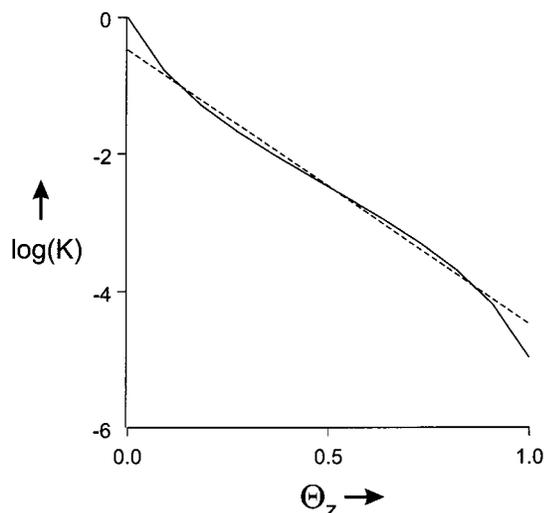


Figure 3. Plot of the natural log of K versus the equivalent fraction of exchanging species calculated for the independent particles in a box, eq 37 (solid) and Kielland plot according to eq 36 with the adjusted parameters $a = -0.476$ and $b = 0.364$ (dotted).

coefficients of the independent particles in a box are equal to 1, it is not justified to use any nonvanishing parameter b for calculating activity coefficients. In the present case, the value of the parameter $b = 0.364$ is due to the decrease of entropy with increasing equivalent fraction of exchanging species (see Table 1). While 36 is a purely empirical equation with no theoretical justification, 37 is the result of a well-defined and simple situation. We therefore suggest that 37 should be used in further studies as a reference for “ideal behavior” and that it is better suited as a basis for defining activity coefficients than the original Kielland equation.

Boxes with Two Different Sites

The sites provided by the unit cell of a microporous material for an ion, an atom, or a molecule are often not equivalent. The interaction of the intercalated species at one site can be stronger than that at another. Such sites can be distinguished by assigning them different occupation probabilities. We therefore devise a system consisting of N_{uc} boxes, each of which can be filled with up to n_{box} particles, as in the previous section. Now, however, m_1 particle positions have an occupation probability q_1 and m_2 have q_2 . The different particle positions correspond to different sites $\sigma = 1, 2$ located in the same box. The following relations hold:

$$\begin{aligned} n_{box} &= m_1 + m_2 \\ 1 &= q_1 + q_2 \\ n_{max} &= m_1 N_{uc} + m_2 N_{uc} \end{aligned} \quad (38)$$

Each time a particle falls in a box on site σ , the probability for a next one to hit that box on site σ decreases by $1/m_\sigma$. This means that once site σ of this box is filled, the probability for a next particle to hit this site becomes zero.

We assume that a total of $n = n_1 + n_2$ particles are already present in our sample. n_1 are the number of particles on site 1 and n_2 those on site 2. Adding $\Delta n = 1$ particles to the sample in a try i causes the number of empty boxes $N_{0,0,i-1}$ to reduce to $N_{0,0,i}$ while the number of boxes $N_{r_1,r_2,i-1}$ containing (r_1, r_2) particles on sites 1 and 2 change to $N_{r_1,r_2,i}$, where $r_1 = 0, 1, \dots, m_1$ and $r_2 = 0, 1, \dots, m_2$. This can be expressed in an analogous way as we did in eqs 5 and 6

$$N_{0,0,i} = N_{0,0,i-1} - (p_{1,0} + p_{2,0})\Delta n N_{0,0,i-1} \quad (39)$$

$$\begin{aligned} N_{r_1,r_2,i} &= \\ N_{r_1,r_2,i-1} &+ p_{1,r_1-1}\Delta n N_{r_1-1,r_2,i-1} + p_{2,r_2-1}\Delta n N_{r_1,r_2-1,i-1} - \\ &(p_{1,r_1} + p_{2,r_2})\Delta n N_{r_1,r_2,i-1} \end{aligned} \quad (40)$$

In these equations, $p_{1,r_1} + p_{2,r_2}$ is the probability that boxes with an occupation (r_1, r_2) vanish by receiving an additional particle on site 1 or 2. $p_{1,r_1-1}\Delta n$ is the probability that boxes containing (r_1-1, r_2) particles are transformed to boxes containing (r_1, r_2) ; the interpretation of $p_{2,r_2-1}\Delta n$ is similar. These probabilities can be expressed in analogy to eq 7 as follows:

$$p_{\sigma,r_s}\Delta n = \frac{\Delta n}{n} \left(\frac{q_\sigma(m_\sigma - r_s)}{(q_1 m_1 + q_2 m_2) - \sum_{r_1=0}^{m_1} \sum_{r_2=0}^{m_2} (q_1 r_1 + q_2 r_2) \frac{N_{r_1,r_2}}{n}} \right), \quad \text{for } \sigma = 1, 2 \text{ and } r_s = r_1, r_2 \quad (41)$$

Using

$$A = (q_1 m_1 + q_2 m_2)n \quad (42)$$

the probabilities p_{σ,r_s} become

$$p_{\sigma,r_s} = \frac{q_\sigma(m_\sigma - r_s)}{A - \sum_{r_1=0}^{m_1} \sum_{r_2=0}^{m_2} (q_1 r_1 + q_2 r_2) N_{r_1,r_2}} \quad (43)$$

The initial conditions when all boxes are empty, as a function of particles n in the sample, of the number of sites (m_1, m_2) in a box, and of the number of unit cells N_{uc} can be written for the particle occupations r_1 and r_2 as follows, in analogy to eqs 11 and 12:

$$N_{0,0}(0, m_1, m_2, N_{uc}) = N_{uc} \quad (44)$$

$$N_{r_1,r_2}(0, m_1, m_2, N_{uc}) = 0 \quad (45)$$

Generalization to three, four, or more different sites is cumbersome but straightforward by extending eqs 38–45 appropriately. It is more useful to discuss the independent particles in a box with two different sites in detail. We do not write differential equations as we did for eqs 5 and 6 because no analytical solution of the problem is known. The occupations $N_{r_1,r_2}(n, m_1, m_2, N_{uc})$ are known, however, from the numerical solution of the problem given in the Appendix B as a Mathcad code that can be translated easily to any other desired form.²²

This ends the mathematical part of the independent particles in a box with two different sites and we now explore its meaning. It is obvious that the systems behavior becomes more complex with respect to the previous case. A given occupation probability set (q_1, q_2) leads to $(m_1 + 1)(m_2 + 1)$ different plots of the type shown in Figure 1. We investigate this for a specific case where we again consider microcrystals consisting of a certain number of boxes each of which bears $n_{box} = 12$ places. $m_1 = 7$ of these places bear an occupation probability $q_1 = 0.25$, and the other $m_2 = 5$ places bear one of $q_2 = 0.75$. We do not show all 48 situations. The four cases illustrated in Figure 4 are sufficient to explain the variety of situations created by two different sites. It is not difficult to understand the system and to derive specific information for any possible situation,

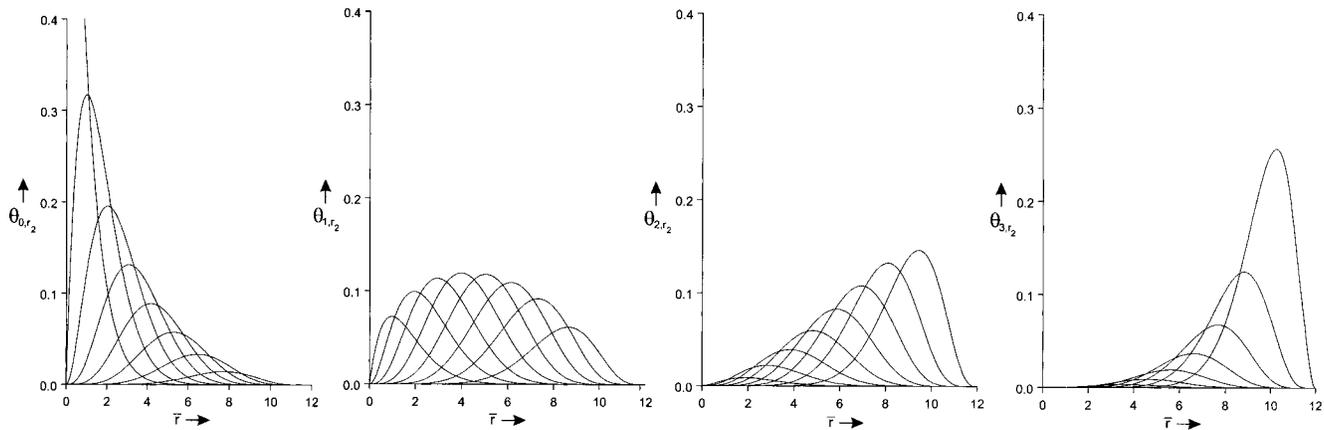
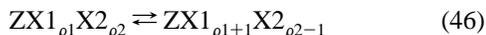


Figure 4. Particle distribution θ_{r_1, r_2} ($r_1 = 0, 1, 2,$ and 3) for the independent particles in a box with two different sites as a function of the mean exchange degree \bar{r} . Each box consists of a total of 12 sites, out of which seven have a probability 0.25 and five have a probability of 0.75 for being occupied. Each plot shows the particle distribution for $r_2 = 0, 1, 2, \dots, 7$ from left to right.

TABLE 2: Distribution of the Particles among the Sites 1 and 2 for an Average Exchange Degree of $r = 5$

| $\rho_2 \backslash \rho_1$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|----------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 0 | 9.8×10^{-4} | 0.008 | 0.031 | 0.064 | 0.078 | 0.057 | 0.023 | 0.004 |
| 1 | 0.002 | 0.013 | 0.048 | 0.097 | 0.118 | 0.086 | 0.034 | 0.006 |
| 2 | 9.2×10^{-4} | 0.008 | 0.029 | 0.059 | 0.072 | 0.052 | 0.021 | 0.004 |
| 3 | 2.8×10^{-4} | 0.002 | 0.009 | 0.018 | 0.022 | 0.016 | 0.006 | 0.001 |
| 4 | 4.3×10^{-5} | 3.7×10^{-4} | 0.001 | 0.003 | 0.003 | 0.002 | 9.3×10^{-4} | 1.6×10^{-4} |
| 5 | 2.6×10^{-6} | 2.2×10^{-5} | 8.1×10^{-5} | 1.6×10^{-4} | 2.0×10^{-4} | 1.4×10^{-4} | 5.5×10^{-5} | 9.4×10^{-6} |

despite its complexity. We observe as an example in the θ_{0, r_2} plot how the unoccupied sites vanish with increasing average exchange degree $\bar{r} = r_1 + r_2$ and how site 2, which has higher occupation probability than site 1, is first occupied by only one particle. However, occupation with two particles starts very soon, and all boxes with only site 2 occupied vanish rapidly above an average exchange degree of about 5. These results can be used for understanding the internal occupation equilibrium 46 of a system with two different sites, 1 and 2, and they are very useful when studying, e.g., spectroscopic properties of species that depend on site occupation probability.



$$K_{\rho_1 \rho_2} = \frac{[\text{ZX1}_{\rho_1+1} \text{X2}_{\rho_2-1}]}{[\text{ZX1}_{\rho_1} \text{X2}_{\rho_2}]} \quad (47)$$

Since all $N_{r_1, r_2}(n, m_1, m_2, N_{\text{uc}})$ are known from the numerical solution of eqs 39 and 40, all individual equilibrium constants $K_{\rho_1 \rho_2}$ can be calculated by means of eq 48, and therefore the change of entropy is known, similarly as in eqs 24 and 25.

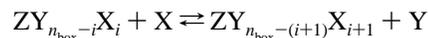
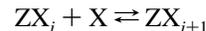
$$K_{\rho_1 \rho_2} = \frac{N_{\rho_1+1, \rho_2-1}}{N_{\rho_1, \rho_2}} \quad (48)$$

A question often encountered concerns the distribution of particles among the different sites for a specified average degree of exchange $\bar{r} = r_1 + r_2$. This information can be extracted from the results illustrated in Figure 4. We show as an example in Figure 5 the results obtained for $\bar{r} = 4$ and 8 and in Table 2 those for $\bar{r} = 5$. It is easy to realize that by playing with the average exchange degree, a number of specific situations can be generated. This can be used for analyzing experimental data and for planning site-specific experiments.

Conclusions

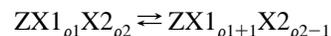
We have explained the independent particles in a box case in detail, and we have shown that the results obtained for this

simple system lead to a thermodynamic description of the following equilibria, relevant in microporous material,



for which the equilibrium constants and the change of entropy have been calculated. This description has successfully been used by us to study the dependency of the electronic spectra of activated $\text{Ag}^{+}_{12-x} \text{M}^{+}_x [\text{Al}_{12} \text{Si}_{12} \text{O}_{48}]$ on the exchange degree x .¹⁹ Our results have been compared with the so-called Kielland plot, which has been generally accepted to be useful for discussing activities in ion exchange equilibria in zeolites, clay minerals, and other materials. We have shown, however, that this choice is quite arbitrary and we propose to substitute it by the independent particles in boxes equation as a reference for "ideal behavior".

The sites provided by the unit cell of a microporous material for an ion, an atom, or a molecule are often not equivalent. They can be distinguished by assigning different occupation probabilities. We have therefore generalized the theory for boxes with unequal sites, and we have illustrated how the fast increasing complexity of the system can be handled for boxes with two different sites, corresponding to the following internal equilibrium in which X1 and X2 are the same species but coordinated to the sites 1 and 2, respectively:



Our results demonstrate the usefulness of the independent particles in boxes with several sites for studying properties of microporous material as a function of the average exchange degree, an experimentally easy to control parameter that therefore plays an important role in many studies of such material.

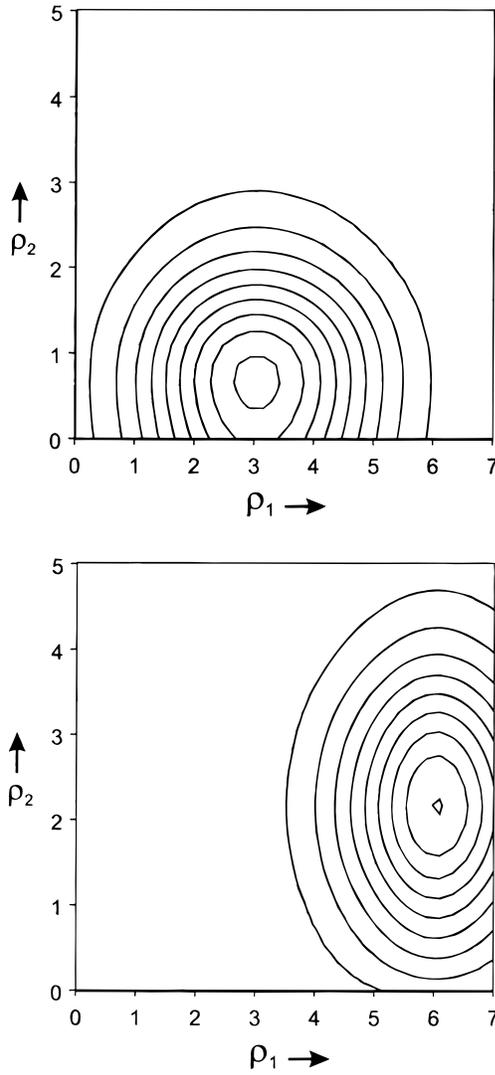


Figure 5. Distribution of the particles among the sites 1 and 2 for an average exchange degree of 4 (upper) and 8 (lower). The values of the maximum contour are 0.120 (upper) and 0.132 (lower) and the spacings between the two contours are 0.013 (upper) and 0.015 (lower).

We conclude that the independent particles in boxes with one ore with several sites facilitates the discussion of relevant observations and the planning of new experiments. It should therefore be considered as a reference system for “ideal site occupation equilibria” in microporous systems.

Appendix

A. Solution of the Independent Particle eqs 9 and 10. To solve this problem we write the eqs 9 and 10 as differential equations A1 and A2 with the initial conditions A3 and A4.

$$\frac{dN_0}{dn} = -p_0 N_0 \quad (\text{A1})$$

$$\frac{dN_r}{dn} + p_r N_r = p_{r-1} N_{r-1} \quad \text{for } n_{\text{box}} \geq r \geq 1 \quad (\text{A2})$$

$$N_0(0, n_{\text{box}}, N_{\text{uc}}) = N_{\text{uc}} \quad (\text{A3})$$

$$N_r(0, n_{\text{box}}, N_{\text{uc}}) = 0 \quad (\text{A4})$$

The solution of A1 is readily found as follows:

$$\int \frac{dN_0}{N_0} = - \int p_0 dn \quad (\text{A5})$$

Using eq 7 for $r = 0$ leads to

$$\ln(N_0) = - \int \frac{n_{\text{box}}}{n_{\text{box}} N_{\text{uc}} - n} dn = n_{\text{box}} \ln(n_{\text{box}} N_{\text{uc}} - n) + \ln C_0 \quad (\text{A6})$$

This equation can be written as

$$N_0 = C_0 (n_{\text{box}} N_{\text{uc}} - n)^{n_{\text{box}}} \quad (\text{A7})$$

We will see later that the integration constant C_0 follows from the initial conditions. To find the solution of A2 we proceed as follows. First, we solve it for the special cases N_1 and N_2 . From this, it will be easy to guess the general solution for N_r , which can be tested by inserting it into A2. Applying the initial conditions will then lead to the solution of the problem. For $r = 1$, we obtain

$$\frac{dN_1}{dn} + \frac{n_{\text{box}} - 1}{n_{\text{box}} N_{\text{uc}} - n} N_1 = \frac{n_{\text{box}}}{n_{\text{box}} N_{\text{uc}} - n} N_0 \quad (\text{A8})$$

$$\frac{dN_1}{dn} + \frac{n_{\text{box}} - 1}{n_{\text{box}} N_{\text{uc}} - n} N_1 = \frac{n_{\text{box}}}{n_{\text{box}} N_{\text{uc}} - n} C_0 (n_{\text{box}} N_{\text{uc}} - n)^{n_{\text{box}}} \quad (\text{A9})$$

The solution of this equation can be expressed as follows:

$$N_1 = G(n) e^{U(n)} \quad (\text{A10})$$

where

$$U(n) = - \int \frac{n_{\text{box}} - 1}{n_{\text{box}} N_{\text{uc}} - n} dn = (n_{\text{box}} - 1) \ln(n_{\text{box}} N_{\text{uc}} - n) + C_{11} \quad (\text{A11})$$

and

$$G(n) = \int \frac{n_{\text{box}}}{n_{\text{box}} N_{\text{uc}} - n} C_0 (n_{\text{box}} N_{\text{uc}} - n)^{n_{\text{box}}} e^{-U(n)} dn$$

$$G(n) = \int n_{\text{box}} C_0 (n_{\text{box}} N_{\text{uc}} - n)^{n_{\text{box}}-1} e^{-[(n_{\text{box}}-1) \ln(n_{\text{box}} N_{\text{uc}} - n) + C_{11}]} dn$$

$$G(n) = n_{\text{box}} C_0 \int e^{-C_{11}} dn = (n + C_{10}) n_{\text{box}} C_0 e^{-C_{11}} \quad (\text{A12})$$

Inserting this into eq A10 leads to

$$N_1 = (n + C_{10}) n_{\text{box}} C_0 e^{-C_{11}} e^{(n_{\text{box}}-1) \ln(n_{\text{box}} N_{\text{uc}} - n) + C_{11}}$$

$$N_1 = n_{\text{box}} C_0 (n + C_{10}) (n_{\text{box}} N_{\text{uc}} - n)^{(n_{\text{box}}-1)} \quad (\text{A13})$$

The solution for N_2 is found by the same procedure as

$$N_2 = n_{\text{box}} (n_{\text{box}} - 1) C_0 \left(\frac{n^2}{2} + n C_{10} + C_{20} \right) (n_{\text{box}} N_{\text{uc}} - n)^{n_{\text{box}}-2} \quad (\text{A14})$$

On the basis of the solutions for N_0 , N_1 , and N_2 it is not difficult to estimate the general solution for $N_r = N_r(n, n_{\text{box}}, N_{\text{uc}})$ to be as follows:

SCHEME 1: Numerical Solution of the Independent Particle in a Box with Two Different Sites

Counting the sites and Abbreviation: $N_{tot} := N_{uc} \cdot (m_1 + m_2)$ $n := 0..N_{tot}$ $A := (q_1 \cdot m_1 + q_2 \cdot m_2) \cdot N_{uc}$

Initial condition, all sites are empty: $N_{empty} :=$ for $r_1 \in 0..m_1$
for $r_2 \in 0..m_2$
 $C_{r_1, r_2} \leftarrow 0$
 $C_{r_1, r_2} \leftarrow N_{uc}$ if $r_1 + r_2 = 0$
C

Calculation of the occupation for two different sites: $N_{occ} :=$ $B_0 \leftarrow N_{empty}$
for $k \in 0..N_{tot}$
 $C \leftarrow B_k$
 $denom \leftarrow A - \sum_{s_1=0}^{m_1} \sum_{s_2=0}^{m_2} (q_1 \cdot s_1 + q_2 \cdot s_2) \cdot C_{s_1, s_2}$
 $numer_1 \leftarrow \frac{q_1}{denom}$
 $numer_2 \leftarrow \frac{q_2}{denom}$
for $r_1 \in 0..m_1$
 $p1_{r_1} \leftarrow (m_1 - r_1) \cdot numer_1$
for $r_2 \in 0..m_2$
 $p2_{r_2} \leftarrow (m_2 - r_2) \cdot numer_2$
for $r_1 \in 0..m_1$
for $r_2 \in 0..m_2$
 $value \leftarrow (1 - p1_{r_1} - p2_{r_2}) \cdot C_{r_1, r_2}$
 $D_{r_1, r_2} \leftarrow$ value if $(r_1 + r_2) = 0$
 $((p2_{r_2-1} \cdot C_{r_1, r_2-1} + value))$ if $[(r_1 = 0) + (r_2 \neq 0)] = 2$
 $(p1_{r_1-1} \cdot C_{r_1-1, r_2} + value)$ if $[(r_2 = 0) + (r_1 \neq 0)] = 2$
 $(p1_{r_1-1} \cdot C_{r_1-1, r_2} + p2_{r_2-1} \cdot C_{r_1, r_2-1} + value)$ if $(r_1 \cdot r_2) > 0$
 $B_{k+1} \leftarrow D$
B

Rearranging the values for more convenient use: $M :=$ for $i \in 0..m_2$
for $r_1 \in 0..m_1$
for $n \in 0..N_{tot}$
 $MM_{n, r_1} \leftarrow \left[\binom{N_{occ}}{n} \right]_{r_1} \cdot \frac{1}{N_{uc}}$
 $B_i \leftarrow MM$
B

Number of boxes, number of sites and site preferences: $N_{uc} = 100$ $m_1 = 7$ $m_2 = 5$ $q_1 = 0.75$ $q_2 = 1 - q_1$

$$N_r(n, n_{box}, N_{uc}) = \frac{n_{box}! C_0}{(n_{box} - r)!} (n_{box} N_{uc} - n)^{n_{box} - r} \sum_{i=0}^r C_{r0} \frac{n^{r-i}}{(r-i)!} \quad C_{r0} = 0 \text{ for } r > 0 \quad (A16)$$

(A15)

From this follows

$$\sum_{i=0}^r C_{r0} \frac{n^{r-i}}{(r-i)!} = \frac{n^r}{r!} \quad (A17)$$

where C_{00} is equal to 1. The validity of A15 can be tested by inserting it into A2. It is easy to see that the initial conditions A3 and A4 are fulfilled if

$$C_0 = \frac{N_{uc}}{(n_{box} N_{uc})^{n_{box}}}$$

$$C_{00} = 1$$

Inserting this in eq A15 leads to the solution expressed in eq 13.

B. Numerical Solutions of The eqs 39–45. The solution of this problem is illustrated in Scheme 1 as a Mathcad file. Where possible, the same symbols have been used as in the text.²²

Acknowledgment. This work was supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Project NF 2000-046617.96/1 and by the Bundesamt für Energiewirtschaft, Project 10441. We thank Dr. Niklaus Gfeller and Dominik Brühwiler for helpful discussions.

References and Notes

- (1) Kielland, J. J. *Soc. Chem. Ind.* **1935**, 54, 232.
- (2) Gaines, G. L., Jr.; Thomas, H. C. *J. Chem. Phys.* **1953**, 21, 714.
- (3) Barrer, R. M.; Rees, L. V. C.; Shamsuzzoha, M. *J. Inorg. Nucl. Chem.* **1966**, 28, 629.
- (4) Sherry, H. S.; Walton, H. F. *J. Phys. Chem.* **1967**, 71, 1457.
- (5) Barrer, R. M.; Davies, J. A.; Rees, L. V. C. *J. Inorg. Nucl. Chem.* **1968**, 30, 3333.
- (6) Breck, D. W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974.
- (7) Van Dun, J. J.; Mortier, W. J. *J. Phys. Chem.* **1988**, 92, 6740. Van Dun, J. J.; Dhaeze, K.; Mortier, W. J. *J. Phys. Chem.* **1988**, 92, 6747.
- (8) Calzaferri, G.; Gfeller, N. *J. Phys. Chem.* **1992**, 96, 3428.
- (9) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *J. Am. Chem. Soc.* **1993**, 115, 10438.
- (10) Jeevanandam, P.; Vasudevan, S. *J. Phys. Chem. B* **1998**, 102, 3082.
- (11) Devautour, S.; Vanderschueren, J.; Giuntini, J. C.; Henn, F.; Zanchetta, J. V.; Ginoux, J. L. *J. Phys. Chem. B* **1998**, 102, 3749.
- (12) Hess, V. L.; Szabo, A. *J. Chem. Educ.* **1979**, 56, 289.
- (13) Ozin, G. A.; Özkar, S.; Stucky, G. D. *J. Phys. Chem.* **1990**, 94, 7562.
- (14) Lainé, P.; Lanz, M.; Calzaferri, G. *Inorg. Chem.* **1996**, 35, 3514. Müller, B.; Calzaferri, G. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 1633.
- (15) Brühwiler, D.; Gfeller, N.; Calzaferri, G. *J. Phys. Chem.* **1998**, 102, 2923.
- (16) Li, J.; Pfanner, K.; Calzaferri, G. *J. Phys. Chem.* **1995**, 99, 2119.
- (17) Kim, Y.; Seff, K. *J. Phys. Chem.* **1978**, 82, 1071.
- (18) Thoni, W. *Z. Kristallogr.* **1975**, 142, 142.
- (19) Seifert, R.; Kunzmann, A.; Calzaferri, G. *Angew. Chem.* **1998**, 110, 1603; *Angew. Chem., Int. Ed. Engl.* **1988**, 37, 1521.
- (20) Meschkowski, H. *Wahrscheinlichkeitsrechnung*; BI Hochschultaschenbücher, Bibliographisches Institut AG: Mannheim 1968.
- (21) Dubler, Th.; Maissen, C.; Calzaferri, G. *Z. Naturforsch.* **1976**, 31b, 569.
- (22) A program PARTIV2 is available at <http://iacrs1.unibe.ch>, 1998.