

MIXED-LAYER MINERALS AS ONE-DIMENSIONAL CRYSTALS¹

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ABSTRACT

If the interaction energy between layers in a mixed-layer crystal depends only on the nearest neighbors, and if the excess interaction energy between unlike neighbors is a constant w , then the mixed-layer crystals can be approximated by the one-dimensional Ising model. The equilibrium number of neighbor pairs of all three kinds in a binary (two types of layers) system can be predicted: if the single parameter w is large and positive, segregation into discrete crystals results; if w is large and negative, unlike layers tend to alternate, forming a regular 1:1 mixed-layer crystal for equal proportion of the two layers. Intermediate values of w result in irregular mixed-layer crystals; only if $w=0$ does a truly random mixed-layer crystal ensue.

The Ising model pertains to crystals of infinite length. For crystals of short lengths, the mathematical approximation of infinite length may be invalid. The correction factor has been calculated for binary, 50-50 systems, up to a total of 16 layers; for thicker crystals the correction is less than 25%.

For many natural and synthetic crystals, the stacking sequences of the layers have been worked out by analysing the X-ray diffraction patterns and intensities. For other crystals, the probabilities p_{ij} of layer succession have been determined by means of the MacEwan method of direct Fourier transform. Using these data, the values of the interaction energy and the excess chemical potentials of mixing are computed. The interaction energies, either positive or negative, are on the order of a few hundred calories per mole of AB neighbor pairs; they may be regarded as the interphase interface energies.

To the extent that the Ising model is applicable, mixed-layer crystals should be regarded as thermodynamically single phases; this conclusion bears on the phase equilibrium study of mineral assemblages involving such crystals. The disappearance of mixed-layer minerals in the diagenesis of sediments and young sedimentary rocks should be a good early indicator of the "metamorphic" grade of the rock.

INTRODUCTION

The stacking sequences in mixed-layer crystals have been studied by many investigators. Most of these studies are concerned with pure description or with the statistics of mixing two or more types of layers in a sequence (*e.g.* Lifshitz, 1937; Hendricks and Teller, 1942; Méring, 1949); the energetics of the interaction between layers was recently considered briefly by Sato (1965). Although both Hendricks and Teller and MacEwan, *et al* (1961) considered the possibility of nonrandom stacking sequences, the possible source of the non-randomness has not been identified.

The one-dimensional Ising model helps in the study of stacking sequences in mixed layer crystals. The model assumes nearest-neighbor interaction with a constant excess interaction energy, and predicts the existence of discrete crystals of the same layer type, regular 1:1 mixed-

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layer crystals, as well as irregular mixed-layer crystals. For this reason, the model serves as a first approximation to real mixed-layer crystals, and provides insight to the causes of development of these various stacking sequences in nature. By producing explicit thermodynamic relations, the model also allows one to make predictions on the properties of those mixed-layer crystals for which direct data are lacking.

A gap exists in conception between: (1) crystallographic parameters measured by X-ray diffraction, and (2) thermodynamic parameters dealing with the energy relations and the phase status of mixed-layer crystals. Because the results of the Ising model can be expressed in terms of run lengths of layer types, which at least in theory are quantities measurable by X-ray diffraction, the model is a direct connection between these two sets of parameters. This feature of the model makes it particularly useful in suggesting directions of further inquiry.

With a few salient exceptions, the statistical-mechanical approach to one-dimensional crystals has dealt with crystals of infinite thickness. When the crystal thickness is finite, the infinite-crystal approximation becomes invalid. A simple method of computing the partition functions of binary mixed-layer crystals of very short lengths has been devised. The results contain some interesting features. For instance, the statistical distribution of the various types of neighbor pairs in a finite chain may not correspond to random distribution even though the excess interaction energy is zero ("ideal mixture"); this stems from the fact that the end effects are significant for short chains. For chains of finite length, therefore, it is necessary to estimate the values not only of the excess interaction energy, but also of the interaction energies of various types of neighbor pairs.

One might object to the present approach to the study of mixed-layer crystals, pointing out that the sequence of stacking of layers might be controlled by kinetic factors of crystal growth rather than by equilibrium considerations: the stacking sequence might reflect, thus, some periodic stacking faults, as exhibited in polytypism of biotite (Ross *et al* 1966), perhaps analogous to screw dislocations (see discussion by Verma and Krishna, 1966, p. 319) which originated during the initial stages of crystal growth. Such stacking faults are examples of long-range forces, outside of the domain of the Ising model; we do not yet know the importance of stacking faults as control of stacking in mixed-layer minerals.

A particular stacking sequence may be the result of accident of crystal growth, or inherited from some pre-existing crystal. If the mixed-layer crystal is not in internal, homogeneous equilibrium, of course, no thermodynamic model, however sophisticated, can be used to describe it; but if homogeneous equilibrium does prevail, a model such as the present

one is useful for comparison against the real stacking sequence. This is true, regardless of whether the equilibrium is stable or metastable, and regardless of the origin of the stacking sequence. Let it be emphasized that the Ising model is not necessarily the correct one for a given mixed-layer crystal; however, it is one step beyond the commonly but tacitly held assumptions that the stacking sequence of mixed-layer crystals is either random or so influenced by unknown factors that it is beyond the realm of rational study. The former assumption we now know to be false, and the body of information on the apparent regularity of stacking of many types of mixed-layer crystals, some of which are cited in this paper, indicates that the latter view is too pessimistic.

FORMAL RELATIONS

General remarks. In this section of the paper, we examine the formal problem of mixed-layer crystals in the light of the Ising model and deduce some of its consequences. Only systems containing two recognizable types of layers, chemically and/or structurally distinct, will be examined; for simplicity they will be referred to as "binary" systems. Two distinct categories of mixed layering should be differentiated because they present different mathematical problems. The first category is mixed layering in which each of the two types of layers, A and B, retains its identity. If N_A and N_B denote the numbers of the two types of layers, then the restrictive conditions are:

$$N_A + N_B = N = \text{constant} \quad (1a)$$

and

$$N_A = \text{constant} \quad (1b)$$

Among examples of minerals having two types of layers are dolomite and the mixed-layer clay minerals.

The second category of mixed layering is one in which the two types of layers are interconvertible, being mutually distinguished only by the spatial orientation of the successive layers: designating one orientation as layer type A and the other orientation as layer type B, we allow the proportions and sequence of the two orientations to vary. The restrictive condition then reduces to (1a) alone. The term "polytypism" has been applied to this type of mixed layering; examples are the various solid SiC phases and ZnS phases, as well as biotite (Ross, Takeda, and Wones, 1966). In this paper, we consider only the first category.

It might be argued that because layers are two-dimensional objects, their stacking cannot be regarded as a one-dimensional problem. However, if the two types of layers cannot interchange material between

them, and if the layers are sufficiently large so that edge effects can be ignored, then the crystal can be fully characterized by the sequence of stacking of the layers in a single dimension. It is, of course, necessary that the two types of layers have the same overall electric charge, so that interchanging two unlike layers does not lead to electric repulsion: we do not, for instance, regard chlorite as a mixed-layer mineral, composed of the talc-like layers (charge -1) and the brucite-like layers (charge $+1$).

Definition of symbols used.

- A, B = Labels identifying two chemically and/or structurally distinct types of layers in an Ising crystal
- F, F_A, F_B = Equilibrium number of runs of A or B
- $K(N)$ = The quasi-chemical "equilibrium constant" relating $\overline{N_{AA}}$, $\overline{N_{BB}}$ and $\overline{N_{AB}}$ as a function of N
- L_A = The length of a run in A
- \overline{L}_A = The average equilibrium length of runs in A
- N = The total number of layers of all kinds
- N_A, N_B = The number of layers of A and B
- $\overline{N_{ij}}$ = The equilibrium number of neighbor pairs between i and j for given N ($i, j = A, B$)
- $\overline{N_{ij}^0}$ = The number of $\overline{N_{ij}}$ at the limiting condition of total segregation of layers
- Q = The partition function
- Q_0 = The configurational partition function for an ideal system
- R = The gas constant
- T = The absolute temperature
- W = The excess interaction energy between the AB type of layers, per mole of neighbor pairs
- i, j = Dummy indices for A and B
- k = The Boltzmann constant
- m = The number of AA type of neighbor pairs in a particular configuration of $N_A + N_B$ layers
- n = The number of AB type of neighbor pairs in a particular configuration of $N_A + N_B$ layers
- p_{ij} = The probability coefficient of an i th layer being followed in a specified direction by a j th layer ($i, j = A, B$)
- w = The excess interaction energy between the A-type and the B-type of layers per neighbor pair
- w_{ij} = The interaction energy between the i th and the j th type of layers ($i, j = A, B$)
- x_A = The mole fraction of the A-type layer

- z = The number of nearest neighbors for a given particle or layer in the lattice
- β = An abbreviation; see equation (4)
- μ'_A = The excess chemical potential of mixing for the A-type layer
- $\eta = e^{-w_{AB}/kT}$
- $\alpha = e^{-w_{AA}/kT}$
- $\gamma = e^{-w_{BB}/kT}$

Stacking sequences in mixed-layer crystals. Mixed-layer crystals can be classified according to the stacking sequences of the layer units. When two types of layers, A and B, form separate crystals of A and B, a mechanical mixture of two phases results; when A and B form regular 1:1 mixed layering¹, such as in ideal dolomite, the resulting crystal is presumably a single thermodynamic phase. Between these extremes are crystals in which the A and B layers may show (1) a tendency to segregate, (2) completely random mixing, or (3) a tendency to alternate. These categories are, collectively, referred to by clay mineralogists as "random mixed-layer" minerals. The term "random", however, is inappropriate except for situation (2) above; for this reason we will use the term "irregular mixed-layer" minerals.

The various types of stacking can grade into each other; they have been characterized by MacEwan (1956a, p. 97) using the parameter p_{ij} ($i, j = A, B$), and by Hendricks and Teller (1942, p. 156) by the parameter $A^{(ij)}$ and an auxiliary parameter A ; both p_{ij} and $A^{(ij)}$ give the probability that an i -type layer is followed in a specified direction along the lattice by a j -type layer. As will be seen later, these descriptive parameters can be related directly to a quantity w , the nonideal or excess interaction energy between A and B layers, as given by the theory of the Ising model. These various terminological equivalences are collected in Table 1.

The one dimensional Ising model. The Ising model was proposed (Ising, 1925) to explain the behavior of one-dimensional ferromagnets. The two entities are the two orientations of the atomic magnetic spin, as such they are interconvertible and only the total number of atomic magnets remains constant. Rushbrooke subsequently solved the problem of the one-dimensional Ising lattice by means of the grand partition function (see

¹ The case of ABAB . . . is, for our purposes, indistinguishable from ABBABB . . . because the double layer BB can be regarded as a single layer. The same redefinition is possible whenever the same number of layers of each kind is involved in a repeated sequence.

Fowler and Guggenheim, 1952, p. 359-366 for a summary discussion); this solution is therefore applicable¹ to the case where the condition (1b) as well as (1a) is obeyed.

The properties that may be used to characterize the one-dimensional Ising model are as follows:

1. There exist the quantities w_{AA} , w_{BB} , and w_{AB} ($=w_{BA}$), which are the interaction energies respectively between the AA, BB, and AB pairs of particles or layers. These quantities are assumed to be constants, not only independent of T , p , the mole fraction $x_A = N_A/(N_A + N_B)$, and the location of the pair in the lattice, but also independent of the nature of

TABLE 1. CLASSIFICATION OF CLAY MINERALS—TERMINOLOGICAL EQUIVALENCES

Structure type	Interaction energy, w	MacEwan, <i>et al</i> (1961) name	MacEwan parameter p_{aa}	Hendricks and Teller (1942) parameter, A
Discrete crystallites	$+\infty$	mechanical mixture of crystallites	1	+1/4
Non-random irregular mixed layering; segregation	$+\infty > w > 0$	Zonal structure; partially random interstratification	$1/2 < p_{aa} < 1$	$+1/4 > A > 0$
Random mixed layering	0	Random interstratification	1/2	0
Non-random irregular mixed layering; alternation	$0 > w > -\infty$	Partially random interstratification with tendency to alternation	$0 < p_{aa} < 1/2$	$0 > A > -1/4$
Regular 1:1 mixed layering	$-\infty$	Alternating regular interstratification	0	-1/4

the neighbors that adjoin a given pair of layers. This last assumption implies that only nearest neighbor interaction is considered in the model.

2. The excess energy of interaction between unlike layers is defined by the relation

$$w = w_{AB} - (w_{AA} + w_{BB})/2 \quad (2)$$

this quantity is also a constant.

3. There exists a one-dimensional lattice along which are located posi-

¹ The grand partition function refers to a system in which the components are perfectly mobile or "boundary value components" (Zen 1963, p. 930); the values of the chemical potentials of the components are externally controlled. The grand partition function considers a problem in which the chemical potentials of the components are equilized between the "system" (a canonical system) of interest and the infinite reservoir of equivalent systems. The different types of layers can be considered therefore as moving in and out of the canonical system until the desired relative proportions of the layers specified in the problem obtains.

tions for the layers or particles (Fig. 1). Each position must be occupied by one and only one particle (a "particle" could be a vacancy, however; this corresponds to the problem of linear surface adsorption). The positions are all equivalent, though the actual location of the point may shift slightly along the lattice to accommodate layers or particles of different sizes. The location of the position, per se, does not impose a bias on the type of particle or layer that occupies it.

Accepting these simple physical assumptions, the equilibrium configuration of the A and B layers can be solved rigorously by means of the grand partition function, from which all the equilibrium thermodynamic

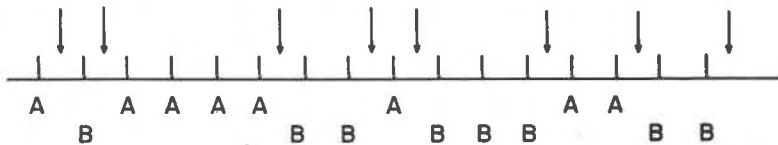


FIG. 1. A schematic representation of the one-dimensional Ising crystal: an infinite chain of equivalent lattice positions each occupied by one, and only one, particle (or layer). The forces between particles extend only to the nearest neighbors, of which there are two for each particle. In the example, there are 16 positions, occupied by 8 layers of A and 8 layers of B. There are 4 runs in A, and 4 runs in B; there are 4 AA neighbor pairs, 4 BB neighbor pairs, and 8 AB neighbor pairs, indicated by arrows (because the chain is infinite, the neighbor pair at the left end is not counted).

parameters can be obtained. For instance, the excess chemical potential of component A, μ'_A , is (Fowler and Guggenheim, 1952, p. 360):

$$\mu'_A = kT \ln \frac{\beta - 1 + 2x_A}{x_A(1 + \beta)} \tag{3}$$

where

$$\beta = [1 + 4x_A x_B (e^{2w/kT} - 1)]^{1/2} \tag{4}$$

(note that for $w=0$, $\mu'_A=0$), from which the entropy of mixing can be obtained by differentiation. As Fowler and Guggenheim pointed out (1952, p. 358), for $w \neq 0$ the entropy of mixing must differ from its ideal value.

The average numbers of AA, BB, and AB neighbor pairs for any value of w is given by (Rushbrooke, 1951, p. 300)

$$\begin{aligned} K(\infty) &= \overline{N_{AA}} \overline{N_{BB}} / \overline{N_{AB}}^2 \\ &= \frac{1}{4} \exp(2w/kT) \end{aligned} \tag{5}$$

where the notations, $\overline{N_{AA}}$, etc., refer to the equilibrium (i.e. the statis-

tically most probable) values of N_{AA} etc. along the chain. Equation (5) resembles the form of the Mass Action Law for chemical reactions; for this reason the model is a special case of the so-called "quasi-chemical" model. The resemblance has a physical basis, for the formation of AB pairs in an infinite chain can be written as a reaction



with an accompanying change in the energy of the system equal to $-2w$.

Equation (5) predicts that for $w=0$, $K(\infty)=1/4$. For $w>0$, $\exp(2w/kT)>1$, so that like-neighbor pairs are preferred. This is the situation of "segregation" of layer types; in the extreme case of $w\rightarrow+\infty$, $\overline{N_{AB}}$ becomes vanishingly small relative to $\overline{N_{AA}}$ or $\overline{N_{BB}}$, so that discrete crystals of A and of B result. On the other hand, for $w<0$, $\exp(2w/kT)<1$, and the AB type of neighbor pairs are preferred. This is the situation of "alternation"; in the limiting case of $w\rightarrow-\infty$, $\exp(2w/kT)\rightarrow 0$ and either all the A layers are sandwiched individually between the B layers, or vice versa, depending on which type is more plentiful: if $N_A=N_B$, a regular 1:1 mixed layer crystal results.

In the special case of $N_A=N_B$, because of the relation (6), equation (5) may be written as

$$\left(\frac{\overline{N_{AA}}}{\overline{N_{AB}}}\right) = \frac{1}{2} \exp(w/kT) \quad (5')$$

We define a "run" as a consecutive sequence of layers of a given type, terminated at each end by a layer of the other type, or by the end of the chain. The length of a run in A is denoted by L_A . The average length of all the L_A 's in the chain is then given by¹

$$\begin{aligned} \overline{L}_A &= \sum_{i=1,2,3,\dots} a_i L_A(i) / F_A \\ &= N_A / F_A \end{aligned} \quad (7)$$

where F_A is the most probable, or equilibrium number of runs in A in the chain and a_i is a weighting factor, proportional to the frequency of occurrence of runs of length L_A . For a binary system of equal proportions, $\overline{L}_A = \overline{L}_B$; if in addition $w=0$, $\overline{L}_A = 2$ according to (5').

The problem of one-dimensional lattices of infinite length and $w=0$ has been examined by Chayes (1957, 1958) using a purely statistical approach. Chayes' results are in accord with those derived from the Ising model by setting $w=0$.

¹ The quantity \overline{L}_A is, strictly speaking, a double average, because it refers not only to average of all the runs in a given configuration, but also the average over all a priori equally probable configurations.

Deducing thermodynamic parameters of mixing from run length. Let F_A , as before, be the equilibrium number of runs in A. In a chain of infinite length where the end effects can be ignored, $F_A = F_B = F$, and the total number of runs of both kinds is $2F$. Moreover, $2F = \overline{N_{AB}}$.

The number of AA neighbor pairs in each run of A, of length L_A , is $L_A - 1$. Therefore, $\overline{N_{AA}} = (\overline{L}_A - 1) \cdot F$, where $\overline{L} = N_A/F$. Likewise, we have $\overline{L}_B = N_B/F$, and $\overline{L}_B - 1 = \overline{N_{BB}}/F$. Substituting these relations into equation (5), and remembering that $\overline{L}_A/\overline{L}_B = N_A/N_B = x_A/x_B$, we get

$$\begin{aligned} K(\infty) &= (\overline{L}_A - 1)(\overline{L}_B - 1)F^2/(2F)^2 \\ &= \frac{1}{4} \exp(2w/kT) \end{aligned} \quad (8)$$

and

$$\begin{aligned} (\overline{L}_A - 1)(\overline{L}_B - 1) &= (\overline{L}_A - 1) \left(\frac{x_B}{x_A} \overline{L}_A - 1 \right) \\ &= \exp(2w/kT) \end{aligned} \quad (9)$$

Solving the quadratic equation for \overline{L}_A , we obtain

$$\begin{aligned} \overline{L}_A &= [1 \pm \sqrt{1 + 4x_A x_B (e^{2w/kT} - 1)}] / 2x_B \\ &= (1 \pm \beta) / 2x_B \end{aligned} \quad (10)$$

Where β is defined by equation (4). For $w \geq 0$, the positive value of the square root is to be chosen; for $w = 0$ it leads to $\overline{L}_A = 1/x_B$, a result also produced by Chayes (1958). For $w < 0$, on the other hand, both roots may be correct, depending on the value of x_A ; for $w \rightarrow -\infty$ the two roots give the values of 1 and x_A/x_B ,¹ which are correct for x_A less than and greater than 0.5, respectively.

For values of $w \neq 0$, either equation (9) or (10) can be used to solve for \overline{L}_A as a function of $2w/kT$ for isopleths in x_A . The relations are most readily portrayed graphically, and are given in Figure 2 (here we plotted $2W/RT$, so that the value of W is the excess interaction energy per mole of neighbor pairs).

We can, moreover, combine equations (3) and (10), to obtain

$$\mu_A' = kT \ln \frac{\overline{L}_A x_B + x_A - 1}{\overline{L}_A x_A x_B} \quad (11)$$

Formulas (9) and (11) provide direct linkages between \overline{L}_A , obtainable

¹ This relation can also be obtained directly by observing that when $\overline{N_{BB}} = 0$, then $\overline{N_{AB}} = 2N_B$.

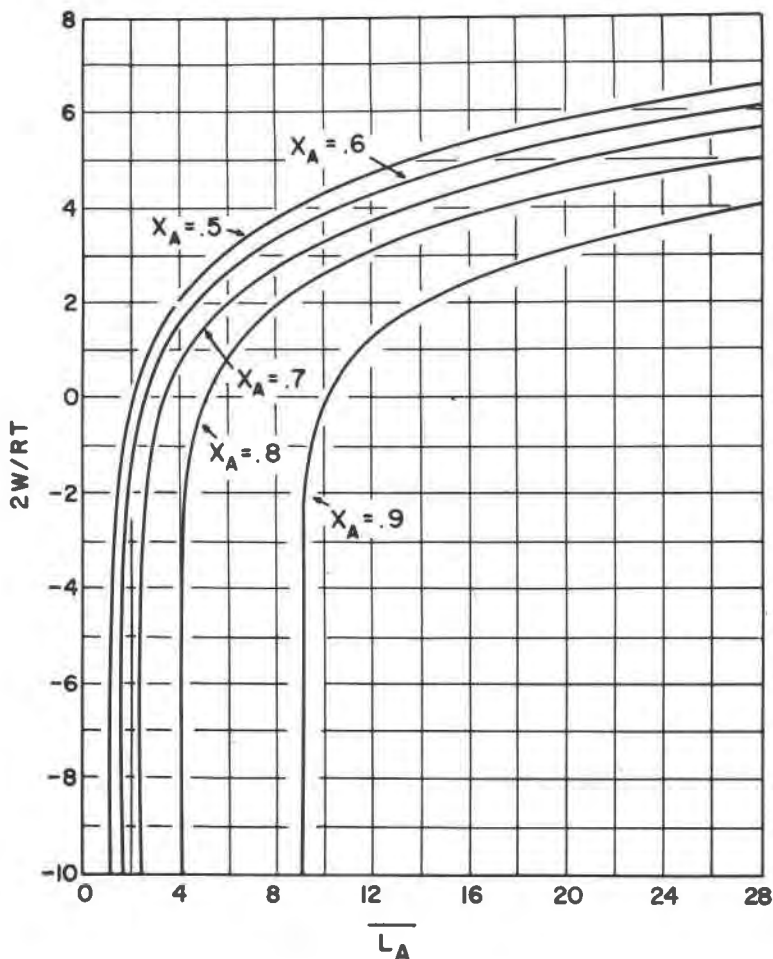


FIG. 2. The quantity $2W/RT$ as a function of the average run length in A, \bar{L}_A , for different values of x_A .

at least in principle from X-ray diffraction data (see APPLICATIONS), and essential thermodynamic parameters for one-dimensional mixed-layer crystals.

Effect of finite crystal size. The statistical mechanics of the one-dimensional Ising model discussed so far assumes the existence of an infinitely long chain. This assumption is fundamental to the mathematical procedure used to compute the partition functions. Chayes' purely statistical run theory for ideal mixtures of particles or layers, likewise, assumes infinitely large samples.

In a real situation, especially for the clay minerals, the validity of the "infinite crystal" assumption is questionable. The "thickness" of clay minerals in the c^* direction is commonly on the order of 0.1 micron or less; this corresponds to approximately 100 layers. Indeed MacEwan (1958) and MacEwan, *et al* (1961, p. 401 ff) computed the X-ray diffraction patterns for 3, 4, 5, and 10 layer clays and found these patterns useful for comparison with real samples! How much error is introduced in using the "infinite crystal" approximation for these crystals?¹

A useful way to measure the error is to calculate $K(N) = \overline{N_{AA}N_{BB}} / \overline{N_{AB}}^2$, which is equation (5) generalized for finite values of N . Let us suppose for the moment that w is zero, i.e., the system is thermodynamically ideal. According to equation (6), $K(\infty) = 1/4$.

The number of distinct ways in which N_A layers of A and N_B layers of B can be arranged in a line is given by the combinatorial formula,

$$Q_0 = (N_A + N_B)! / N_A! N_B! \quad (12)$$

For $w=0$, this number is exactly the configurational partition function for the system. Our task amounts to counting, for a given N_A and N_B , the total number of neighbor pairs of each kind for all configurations, assuming, as is customary, that each configuration of the A and B units along the chain is a priori equally probable. We can then obtain $\overline{N_{AA}}$ etc. readily, because $\overline{N_{AA}} = N_{AA}/Q_0$, etc.

For a chain of finite length, the total average number of neighbor pairs of all kinds no longer equals the total number of layers. Instead we have

$$\overline{N_{AA}} + \overline{N_{BB}} + \overline{N_{AB}} = N_A + N_B - 1 \quad (13a)$$

and also the condition at complete segregation,

$$\overline{N_{AA}}^0 = N_A - 1, \quad \overline{N_{BB}}^0 = N_B - 1, \quad \overline{N_{AB}}^0 = 1 \quad (13b)$$

Unfortunately, we have not solved the general problem of counting $\overline{N_{AA}}$, etc. as a function of N and of x_A , even for the special case of $x_A = 1/2$. Nonetheless, by actually enumerating these quantities $\overline{N_{AA}}$, $\overline{N_{BB}}$, and

¹ NOTE ADDED IN PROOF: Since the writing of the paper, the following references, pertinent to the discussion, have come to my attention: R. W. Rex (1966) Authigenic kaolinite and mica as evidence for phase equilibria at low temperatures, *Clays Clay Miner., Proc. Nat. Conf.* **13**, 95-104; Emerson, W. W. (1962) The swelling of Ca-montmorillonite due to water absorption. I. Water uptake in the vapour phase. *J. Soil Sci.* **13**, 31-39.

² Aside from the fact that the ends of the chain can no longer be ignored, the problem is further complicated by the fact that the location of a layer at a given position affects the probability of occupancy of the next position by a particular type of layer, because the value of x_A is changed by each successive assignment of layers to positions.

$\overline{N_{AB}}$ for such symmetrical cases, for $N=2, 4, 6, 8, \dots, 16$, the values of $K(N)$ are found to follow the relation:

$$\begin{aligned} K(N) &= \overline{N_{AA}} \overline{N_{BB}} / \overline{N_{AB}}^2 \\ &= \left(\frac{1}{2} - \frac{1}{N} \right)^2 \\ &= \frac{1}{4} \left(\frac{N-2}{N} \right)^2 \end{aligned} \quad (14)$$

The factor

$$\left(\frac{N-2}{N} \right)^2$$

is the correction for the finite chain length; it approaches unity as $N \rightarrow +\infty$. The fractional correction is

$$\begin{aligned} \Delta K(N) &= \frac{K(\infty) - K(N)}{K(\infty)} \\ &= 4(N-1)/N^2 \end{aligned} \quad (15)$$

The values of $K(N)$ for unequal numbers of N_A and N_B have also been computed for even N , up to $N=16$. The results, together with those for the symmetrical cases, are presented in Figure 3. It is obvious from the figure that the family of curves is asymptotic to $K(\infty) = 1/4$ regardless of the value of x_A , confirming that equation (5) derived from the grand partition function, is independent of x_A .

For the case of $N_A = N_B$, $w = 0$, and $w_{AA} = w_{BB}$ [see p. 649] we can also compute the average run length as well as the average number of runs in a given sequence, using equation (14). Let F_A be the double-average (equilibrium) number of runs in A for a chain of specified finite length, and let \overline{L}_A be the double-average length of the runs in A; then

$$F_A \overline{L}_A = N_A \quad (16a)$$

$$F_B \overline{L}_B = N_B \quad (16b)$$

and

$$F_A + F_B = N_{AB} + 1 \quad (17)$$

Setting now

$$\begin{aligned} K^{1/2}(N) &= \overline{N_{AA}} / \overline{N_{AB}} \quad (\overline{N_{AA}} = \overline{N_{BB}}) \\ &= \frac{N-2}{2N} \end{aligned} \quad (18)$$

we get

$$F_A = F_B = (N + 2)/4 \quad (19)$$

and

$$\overline{L}_A = \overline{L}_B = N_A/F_A = 2N/(N + 2) \quad (20)$$

which correctly reduces to the value of 2 as $N \rightarrow \infty$.

The formulation of the partition function for nonideal systems having finite chain lengths is difficult. A matrix method (see Hill, 1956, p. 318–327), involving interconvertible entities, has been successfully applied to the helix-coil transition of polypeptides.¹ Krivoglaz and Smirnov (1964, p. 145 ff) discussed a matrix method for binary alloys in 1, 2, and 3-dimensional crystals that uses the grand partition function and is applicable to any value of x_A .

For our purposes, however, a much simpler approach can be used; this involves the direct enumeration of N_{AA} , N_{BB} , and N_{AB} , which can be readily accomplished for small values of N with the aid of a computer. Multiplying both sides of equation (2) by $2/kT$ and taking the exponents, we get,

$$e^{2w/kT} = e^{2w_{AB}/kT} e^{-w_{AA}/kT} e^{-w_{BB}/kT} \quad (2a)$$

which will be abbreviated as

$$e^{2w/kT} = \eta^{-2} \alpha \gamma \quad (2b)$$

As we are interested only in the relative energy values, let us assign the value of unity to γ ; the values of η and α are adjusted accordingly. For a given set of values of x_A , N_A and N_B , we could enumerate all the configurations of A and B along the chain, and, assuming that each configuration is a priori equally probable, calculate the contribution to the partition function from each configuration by assigning to each AA neighbor pair the multiplicative factor α , and to each AB neighbor pair, the factor η . Each configuration will then contribute a term in the form of $\eta^n \alpha^m$, where m and n are the numbers, respectively of the AA and AB neighbor pairs present in that particular configuration; the partition function is in the form of polynomials in η and α . As an example, consider a system in which

¹ In the polytypism of e.g. biotite, where the stacking problem for the layers refers to different orientations of the self-same layers in the ab plane (Ross, Takeda, and Wones, 1966), the different "layers", being just different orientations, are interconvertible. With suitable modifications to account for the symmetry of the layers, the matrix method should be applicable to these problems of polytypism. For this reason, several references to the treatment of the helix-coil transition are included in the reference section: Peller (1959a, b); Zimm and Bragg (1959); Zimm, Doty, and Iso (1959); Lifson and Roig (1961); Applequist (1963); Poland and Scheraga (1965).

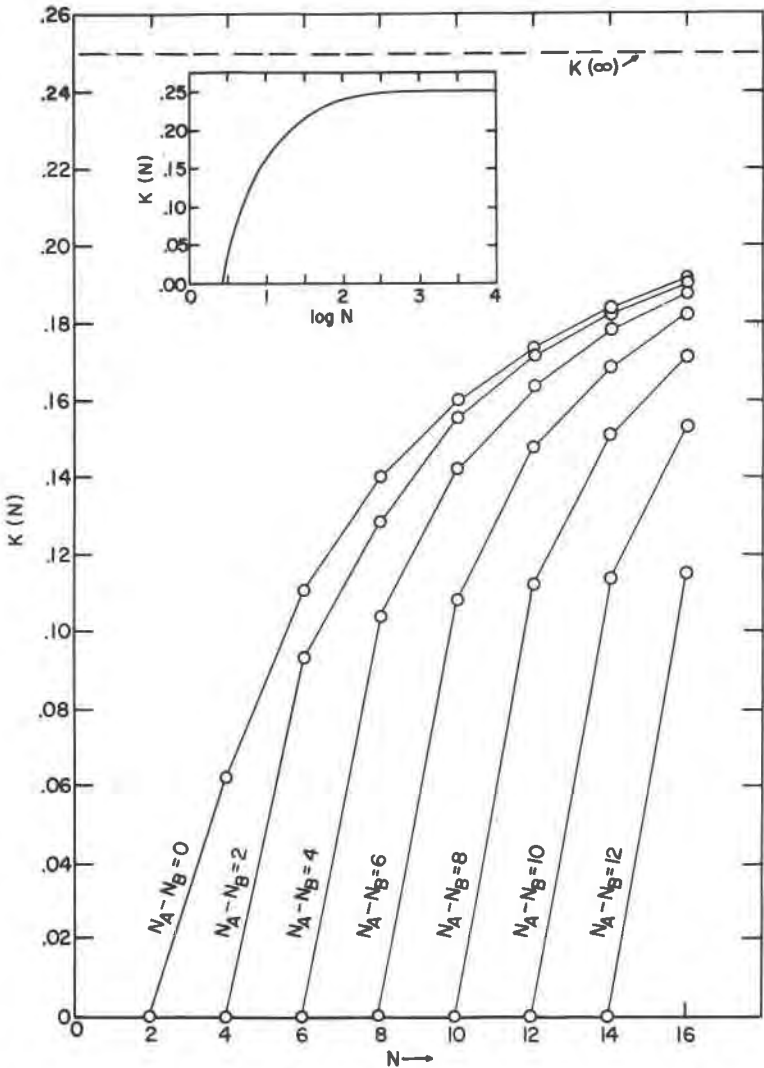


FIG. 3. The asymptotic behavior of $K(N)$. Individual computed values are shown in circles; the straight line segments connecting the circles are meant to aid the eye and have no meaning. Notice that for sufficiently large N , all the curves approach the value of $K(\infty) = \frac{1}{4}$. The inset shows the asymptotic behavior more clearly by using a logarithmic scale so that N is as large as 10^4 . The excess interaction energy is taken to be zero in all cases.

$x_A = 1/2$, and $N_A = N_B = 2$. There are $4!/2!2! = 6$ distinct configurations, namely AABB, ABBA, ABAB, BABA, BAAB, BBAA. Their corresponding contributions to the partition function are $\alpha\eta$, η^2 , η^3 , η^3 , $\alpha\eta^2$, $\alpha\eta$.

TABLE 2. COMPARISON OF VALUES OF $K(N)$ USING DIFFERENT EQUATIONS, FOR $N_A=N_B=2$; IT IS ASSUMED THAT $\gamma=1$ AND $\alpha=0.5$

η^2	0.09	0.5	3.0
η	0.3	0.71	1.73
α/η^2	5.6	1	1/6
$2W/RT = \ln \alpha / \eta^2$	+1.72	0	-1.8
$K(N)$	0.252	0.0617	0.00870
$K(\infty)$ (eq. 5)	1.4	0.250	0.0417
$K'(\infty) = K(\infty) (N-2/N)^2$ (eq. 14)	0.35	0.0625	0.0104
$\Delta K = \frac{100[K'(\infty) - K(N)]}{K'(\infty)}$	29%	1.4%	16%

Therefore, the partition function is

$$Q = 2\alpha\eta + \eta^2 + \alpha\eta^2 + 2\eta^3 \quad (21)$$

We can calculate \overline{N}_{ij} because (see Davidson, 1962, p. 380)

$$\overline{N}_{AA} = (\partial \ln Q / \partial \ln \alpha) \eta \quad (22a)$$

$$\overline{N}_{AB} = (\partial \ln Q / \partial \ln \eta) \alpha \quad (22b)$$

We find that

$$\overline{N}_{AA} = \alpha\eta(2 + \eta)/Q \quad (23a)$$

$$\overline{N}_{AB} = 2\eta(\alpha + \alpha\eta + \eta + 3\eta^2)/Q \quad (23b)$$

so that

$$\overline{N}_{BB} = 3 - \overline{N}_{AB} - \overline{N}_{AA} = \eta(2\alpha + \eta)/Q \quad (23c)$$

and

$$K(4) = \frac{\overline{N}_{AA} \overline{N}_{BB}}{\overline{N}_{AB}^2} \quad (24)$$

$$= \frac{1}{4} \left[\frac{\alpha(2 + \eta)(2\alpha + \eta)}{(\alpha + \eta + \alpha\eta + 3\eta^2)^2} \right]$$

As illustrations, in Table 2 we present the values of K calculated by three methods for the symmetrical 4-layer case, for several arbitrarily chosen values of η , α and γ . We see that the use of equation (14) eliminated the bulk of the discrepancy caused by the infinite-chain assumption. However, the nonideal term contributes further to errors which are not corrected by the use of equation (14). Moreover, the small difference between the values of $K(N)$ from equation (24) and from equation (14) is real and is caused by the nonequality of α and γ ; this apparently stems

from the fact that the quasi-chemical equation (6) is no longer valid and the end-of-chain effect comes into play even where $w=0$.

APPLICATIONS

Problem of defining a "neighbor pair" in a mixed-layer crystal. Our discussions so far have been strictly qualitative, so that it did not matter what individual "neighbor pairs" signify physically. When, however, we attempt to attach numerical values to the quantity w and/or μ , it becomes imperative that the concept of a "neighbor pair" be more clearly stated. Unfortunately, it is not at all obvious, a priori, what physical entity a "neighbor" should correspond to. Clearly it is not the layer itself; for otherwise we should be able to double the number of neighbor pairs (and thus the total excess energy of the system) simply by slicing the crystal in two in a plane normal to the layers, obviously an absurd situation. On the other hand, a "neighbor pair" might correspond to an individual atom or group of atoms that forms the physical connection between adjacent layers. Ignoring edge effect, an acceptable choice of a "neighbor pair" must be independent of the actual dimensions of the layers. If the proper choice of neighbor pair is made, the calculated value of W should lead to a measure of the interface energy between the two types of layers.

Deducing W from X-ray diffraction data; Examples. Equation (5) predicts that segregation of the layers into discrete crystals of different types can happen only when $W \rightarrow +\infty$. In practice, however, the restriction may be much less stringent, as the hypothetical example below indicates.

Consider a sample in which two layer types, A and B, both 10 Å thick and potentially capable of layer mixing, are found as grains of pure A and pure B, in mutual chemical equilibrium. The crystals average 1 mm on the side and the two types of grains occur in equal abundance. There is little doubt that these crystals will be accepted as discrete thermodynamic phases. Now a crystal 1 mm thick contains 10^6 layers, so that if we identify the average grain thicknesses with the quantity \bar{L} , then from equation (8) or figure 2 we obtain $10^{12} \approx \exp(2W/RT)$, and $W/T \approx 27.6$ cal/mole deg. If the equilibrium temperature was 600°K, W becomes 16.6 kcal per mole of \bar{N}_{AB} . However, inasmuch as only one out of 10^6 layers encounters an AB neighbor pair, the excess energy is no more than 0.016 cal per gram atomic formula of the phase. It therefore appears that megascopically discrete crystals, presumably to be identified as phases, can obtain with values of W so small as to be calorimetrically unmeasurable.

Quantitative evaluation of W . MacEwan (1956a) presented a method of direct Fourier transform whereby it is possible to detect from the X-ray

diffraction pattern the presence of such packets of layers as AB, AAB, AAAB, . . . The relative abundances of these packets are derived from the heights and positions of their X-ray diffraction maxima, and lead to numerical estimates of the probability factors p_{ij} ($i, j = A, B$; see Table 1). Because the factors p_{ij} in a binary system are directly proportional to \overline{N}_{ij} , the results of the MacEwan transform lead to estimates of W/RT insofar as the p_{ij} 's thus calculated are good approximations of the true values of the p_{ij} 's. An additional, tacit assumption is that the clay minerals studied can be statistically regarded as infinitely thick crystals.

As an example, a Li-saturated montmorillonite from a Wyoming bentonite (Brown and Greene-Kelly, 1954) contains two types of layers. MacEwan (1956a, p. 103) calculated that $p_{AA} = p_{BB} = 0.33$, $p_{AB} = 0.67$ ($x_A \approx 0.5$). Thus, inasmuch as the AB and BA neighbor pairs are not distinguished in the Ising model, $\overline{N}_{AA} = \overline{N}_{BB} = 0.33f$, and $\overline{N}_{AB} = 1.34f$, where f is a proportionality constant. Substituting into equation (8), we get $2W/RT = -1.4$. If the homogeneous equilibrium was attained at 300°K, W becomes -420 cal per mole of AB neighbor pairs. The negative sign signifies that the layers tend to alternate and the AB neighbor pairs are preferred.

A second example is a clay mineral that consists of two types of layers: vermiculite-like and/or chlorite-like (A) and montmorillonite-like (B), examined by Bradley (1953). MacEwan (1956a, p. 104) showed that $p_{AA} = 0.65$, $p_{BB} = 0.75$, $p_{AB} = 0.35$, and $p_{BA} = 0.25$ ($x_A = 0.43$). Therefore, proportionally $\overline{N}_{AA} = 0.65$, $\overline{N}_{BB} = 0.75$, and $\overline{N}_{AB} = 0.60$. Substitution into equation (8) yields $2W/RT = +1.7$. Assuming an equilibrium temperature of 300°K, $W = +510$ cal per mole of AB neighbor pairs. Note that the mixed layering is between a dioctahedral and a trioctahedral unit; the positive value of W is reasonable because there is considerable difference in the dimensions and atomic arrangements between these two types of layers and work must be performed onto the layers to cause them to fit.

Sato (1965) presented data on the values of p_{ij} for another illite-montmorillonite sample; unfortunately his data are graphically presented and can only be imprecisely interpolated. Nonetheless, approximately $p_{AA} = 0.63$, $p_{BB} = 0.11$, $p_{AB} + p_{BA} = 1.26$, $x_A = 0.71$, so that $2W/RT = -1.2$. Table 3 gives, for the samples of Sato and MacEwan, the values of $2W/RT$, \overline{L}_A , \overline{L}_B , μ'_A/RT , and μ'_B/RT as computed from equations (10) and (11).

Possible examples of $W < 0$. If $W < 0$, unlike layers tend to alternate. All 1:1 regular mixed layer crystals belong to this category. A good example is dolomite, which consists of 1:1 regular mixed layer of CaCO_3 and MgCO_3 , confirmed by recent X-ray structure analysis (Steinfink and Sans, 1959, p. 680)

The MgCO_3 and CaCO_3 layers in the metastable protodolomite are apparently irregularly distributed along the c direction (Graf, Blyth and Stemmler, 1957). The large negative value of W deduced for dolomite suggests that the two types of layers may tend to alternate, and so the value of \bar{L} may lie between 2 (random mixture) and 1 (perfectly ordered alternation). Likewise, it seems reasonable to surmise that layers having compositions approaching CaCO_3 and MgCO_3 exist in the crystals of high-magnesium calcites; these layers presumably tend to alternate so that the MgCO_3 — MgCO_3 neighbor pairs are avoided.

Kohn and Eckart synthesized the hexagonal ferrites, related to magnetoplumbite. These crystals consist of different stackings of two anionic

TABLE 3. CALCULATED $2W/RT$, \bar{L}_A , \bar{L}_B , μ'_A/RT , μ'_B/RT AND RANDOM-MIXING \bar{L}_A , \bar{L}_B (FOR COMPARISON) FOR THREE MIXED-LAYER CLAY MINERALS

Sample	x_A^1	x_B	p_{AA}	p_{BB}	p_{AB} + p_{BA}	$2W/RT$	μ'_A/RT	μ'_B/RT	Run length			
									Computed W		$W=0$	
									\bar{L}_A	\bar{L}_B	\bar{L}_A	\bar{L}_B
1	0.71	0.29	0.63	0.11	1.26	-1.7	-0.13	-1.2	2.7	1.1	3.5	1.4
2	~0.50	~0.50	0.33	0.33	1.34	-1.4	-0.41	-0.41	1.5	1.5	2.0	2.0
3	0.43	0.57	0.65	0.75	0.60	+1.7	+0.42	+0.26	2.9	3.9	1.8	2.3

1. Sato, 1965, Sample B.

2. MacEwan, 1956a, p. 103, Wyoming bentonite.

3. MacEwan, 1956b, p. 104.

¹ x_A and x_B may be calculated where not specified. Useful relations:

$$x_A p_{AA} + x_B p_{BA} = x_A; x_B p_{BB} + x_A p_{AB} = x_B; x_A + x_B = 1; p_{AA} + p_{AB} = 1; p_{BB} + p_{BB} = 1$$

structural layer types, one having the oxygen framework in the spinel configuration (0), and one having 1/4 of the oxygen of the spinel framework replaced by Ba or Pb atoms (Ob). These layers form ordered superlayers in three configurations: S = O—O, R = O—Ob—O, and T = O—Ob—Ob—O (Kohn and Eckart, 1964a, p. 456). The R, S, and T superlayers in turn form three types of layers: M = RS, Y = TS, and RSS.

The M and Y layers, and the M and RSS layers, form two series of ferrites, within each series various permutations of the M and Y (or M and RSS) sequence for given M:Y (or M:RSS) ratios are possible. Kohn and Eckart (1965b, p. 1374) showed that in the magnetoplumbite series, $M_n Y_m$, where $M = (\text{Pb}, \text{Ba})\text{Fe}_{12}\text{O}_{19}$ and $Y = \text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, the observed stacking sequences are such that the M-M neighbor pairs are avoided. The single exception is $M_2 Y$; in this case the stoichiometry requires the existence of M-M neighbor pairs, but N_{MM} is minimized nevertheless by the absence of N_{YY} and the presence, therefore, of maximum

number of N_{MY} . One may conclude that the excess energy W is large and negative between M and Y layers.

In the series composed of RSS and M, the M-M neighbor pairs are present in the polymorph designated 66R (= RSS.M₃ or M₄S) (Kohn and Eckart, 1964b). The neighbor pair RSS·RSS has not yet been recorded in this series; the situation is analogous to that for the MY series.

In magnetoplumbite in the system Ba-Mn-Zn-Fe³⁺-O, in which Mn replaces Zn in part, the M-M neighbor pair has been recorded in crystals having the stacking sequence M₂Y₁₁, such that this neighbor pair is not demanded by the stoichiometry (Kohn and Eckart, 1965a). It appears, therefore, that this cationic substitution increases the algebraic value of W appreciably to permit both M-M and Y-Y type of neighbor pairs; some irregularity in the stacking of M and Y layers may thus be possible. It may be that the nature and possibly the positions of the small ions that do not directly replace oxygen in the framework affect the stack-sequences.

Another example pertains to the "minerals" bastnaesite, parisite, roentgenite, and synchisite (Donnay and Donnay, 1953), having the compositions respectively of CeFCO₃, 2CeFCO₃·CaCO₃, 3CeFCO₃·2CaCO₃, and CeFCO₃·CaCO₃. In detail, layers exist that have the composition CeFCO₃ (= 1) or CaCO₃ (= 2), such that the stacking sequences are respectively 111 . . . ; 112112 . . . ; 2121121211 . . . , and 1212 . . . (Donnay and Donnay, 1953, p. 944). In all the cases, $\bar{N}_{22} = 0$, and \bar{N}_{12} is maximized. The value of W , therefore, must be large and negative.

Other possible examples of mixed-layer crystals are phases in the system AlN-Al₄C₃ (Jeffrey and Wu, 1963), the humite group of minerals (Bragg and Claringbull, 1965, p. 175-178), and staurolite (Náray-Szabó and Sasvári, 1958); the reader is referred to these references.

The bulk of data on mixed-layer crystals showing tendency to maximize unlike neighbor pairs, however, comes from the clay minerals. MacEwan, *et al* (1961) presented an excellent review of the subject up to that time; only a few examples need to be discussed here.

Regular 1:1 mixed-layer clay minerals are known. Allevardite (MacEwan, *et al*, 1961, p. 425) is a 1:1 mixture of muscovite-like and montmorillonite-like layers; corrensite (see Vivaldi and MacEwan, 1960) is a 1:1 mixture of chlorite-like and vermiculite-like layers; rectorite (MacEwan, *et al*, 1961, p. 426) is a 1:1 mixture of pyrophyllite-like and vermiculite-like layers. Hydrobiotite consisting of regular 1:1 alternation of biotite-like and vermiculite-like layers is known (*e.g.*, Bassett, 1959, p. 296). If these clay minerals are in internal homogeneous equilibrium, then in all cases $\bar{N}_{AA} = \bar{N}_{BB} = 0$, $\bar{N}_{AB} = \text{maximal}$, and the value of W must be large and negative.

MacEwan (1956b, p. 166-169) described an illite (A)-montmorillonite (B) clay from Woodbury, Worcestershire, England, showing 72 percent illite-like layers. The X-ray diffraction pattern is matched by a Fourier transform in which is assumed $\overline{N_{BB}}=0$, so that $\overline{N_{AB}}$ is maximum; the distribution of run lengths in A, however, may be random (MacEwan, 1956b, p. 168).

According to MacEwan (1956b, p. 167), several mixed-layer illite (A)-montmorillonite (B) clays ($x_A = .68$) from Kinnekulle, Sweden, described by Byström (1954), have X-ray diffraction patterns similar to that of the Woodbury clay (see, however, discussion by Byström, 1956, p. 29), and the observed patterns are likewise well matched with Fourier

TABLE 4. CALCULATED $\overline{L_A}$ AND $\overline{L_B}$ OF SAMPLES FOR WHICH $W \rightarrow -\infty$

Sample	x_A^1	x_B	p_{AA}	p_{BB}	$p_{AB} + p_{BA}$	$W = -\infty$		$W = 0$	
						$\overline{L_A}$	$\overline{L_B}$	$\overline{L_A}$	$\overline{L_B}$
1	0.71	0.29	0.60	0	1.40	2.4	1	3.5	1.4
2	0.60	.40	.33	0	1.67	1.5	1	2.5	1.7
3	0.60	.40	.33	0	1.67	1.5	1	2.5	1.7
4	0.72	.28	.61	0	1.39	2.6	1	3.6	1.4
5	0.68	.32	.56	0	1.44	2.1	1	3.1	1.5
6	0.72	.28	.61	0	1.39	2.6	1	3.6	1.4

1-3. Sato, 1965, samples A, C, D, respectively, layers are illite-like and montmorillonite-like.

4, 5. MacEwan, 1956b (#3, Woodbury; #4, Kinnekulle).

6. Sato *et al*, 1965. Illite=0.72, montmorillonite=0.28.

¹ See footnote, Table 3.

transforms by assuming $\overline{N_{BB}}=0$ and $\overline{N_{AB}}$ maximum, suggesting that W is large and negative, in agreement with the implications of the regular 1:1 allevardite which is composed of the same types of layers.

D'yakonov (1964) described hydrobiotites in which the biotite-like (A) and vermiculite-like (B) layers differ in proportions. He found that there is a predominance of the AB type of neighbor pairs, and apparently a low value of $\overline{N_{BB}}$. The data are in accord with the existence of 1:1 regular mixed-layer hydrobiotite.

Sato (1965) and Sato *et al* (1965) presented data on additional mixed-layer clay samples in which $p_{jj}=0$, corresponding to values of $W \rightarrow -\infty$. These data, as well as those of MacEwan, are collected in Table 4, in which the calculated values of $\overline{L_A}$ and $\overline{L_B}$ are compared with the value for $W=0$.

The fact that all the illite-montmorillonite mixed-layer clay minerals of this table have p_{BB} (B=montmorillonite)=0 is interesting. This feature may mean that a montmorillonite-like layer requires an illite-like layer on each side to achieve local charge balance; the large negative value of W thus could simply mean that the electric forces overwhelm the relatively weak Van der Waals forces between neutral layers.

Possible examples of $W > 0$. When $W > 0$, the like layers tend to cluster together and unlike layers tend to avoid each other; according to the Ising model, megascopically discrete crystals can be formed if the value of W is numerically sufficiently large.

Such micaceous mineral pairs as biotite and muscovite, biotite and paragonite, muscovite and paragonite, and probably even biotite and chlorite, characteristically occur in nature as discrete crystals. These relations are explicable in terms of the Ising model and large, positive values of W .

Maiklem and Campbell (1965) applied the MacEwan method of Fourier transform to several clay minerals from a Cretaceous bentonite of Alberta, Canada. Their results are ambiguous because of the poor agreement between calculated Fourier intensities, both for random stacking and for maximum alternation, and the observed values. The situation is further complicated by the presence of three types of layers: illite-like (A), vermiculite-like (B), and montmorillonite-like (C) (Maiklem and Campbell, 1965, p. 363). However, it appears that AA, BB, and CC type of neighbor pairs all exist in significant proportions, and in at least one sample (no. 4132; p. 365-366) agreement between calculated and observed intensities is best achieved by assuming the presence of most of the montmorillonite-like layers as a mechanical admixture of montmorillonite crystals. The data of Maiklem and Campbell suggest that the value of W between the montmorillonite-like layers and the other types may be positive.

STATUS OF THE MIXED-LAYER CRYSTALS AS THERMODYNAMIC PHASES

The question of the thermodynamic status of the mixed-layer crystals as phases in the sense of the phase rule has been discussed by mineralogists and has been recently summarized by Zen (1963, p. 938). The problem is pertinent to petrology, because, for example, in studying the equilibrium relations of a mineral assemblage, one must count the number of phases correctly; if the assemblage includes a mixed layer mineral, one must know whether it is one or more phases.

For the one-dimensional Ising model, the critical temperature, T_c ,

for phase separation at the top of the solvus (necessarily at $x_A = 1/2$ because the Ising model is symmetrical with respect to composition) is given by (Fowler and Guggenheim, 1952, p. 360-361)

$$\frac{2w}{kT_c} = Z \ln \frac{Z}{Z-2} \quad (26)$$

where Z is the number of nearest neighbors. For $Z=2$, $T_c=0$ unless $w \rightarrow +\infty$ (the criterion of phase separation used is the thermodynamic one, namely $\partial\mu_A/\partial x_A=0$, and $\partial^2\mu_A/\partial x_A^2=0$), so that, in general, there can be no phase separation for one-dimensional crystals (Landau and Lifshitz, 1958, p. 482).

In the helix-coil transition of polypeptides, however, the abruptness of the transition has been associated with a first order phase transition. Zimm and Bragg (1959, p. 526, 535) noted the novelty of this feature, but showed that the excess interaction energy between the coiled and helical forms is effectively very large. Previously, we have already associated the existence of separate "end member" crystals with values of $W \rightarrow +\infty$; the added feature of equation (26) above is that even the coexistence of two phases along two limbs of a solvus is prohibited for a one-dimensional Ising crystal.

Discrepancies between this prediction and the observed coexistence of, for example, montmorillonite and illite as separate crystals could be caused by one of three factors:

- (a) The discrete crystals are not in mutual equilibrium; given sufficient activation energy, they will react to form a homogeneous phase;
- (b) The Ising model does not apply either because it disregards long-range forces, or because w is not a constant; or
- (c) The Ising model does not apply because the real mixed layer crystals are finite in the other two dimensions, which cannot be ignored.

Errors introduced by the approximation (c) should be minimal if the layers act as chemically closed units. Interlayer exchange of different types of atoms that physically link the layers (e.g., Na and K atoms between muscovite-like layers), however, is entirely conceivable; such an interchange would disturb the interatomic forces within each layer. These correlation effects within layers are not handled by the Ising model as presented here; yet these effects do not make the crystal a two-dimensional Ising crystal either. In addition, in the above example, the distortion of the silicate framework due to differing sizes of the potassium and sodium ions (Burnham and Radoslovich, 1964, p. 235) may also serve to propagate long range forces across the layers. To these extents, then, the one-dimensional Ising model may be a poor approximation of real mixed-layer crystals. In the absence of further information on this

subject, however, it seems best at the present to regard the mixed-layer crystals, for example the mixed-layer clays, as single-phase material.

MIXED-LAYER CLAYS IN NATURE: ISOGRAD INDICATORS?

Among the mixed-layer minerals that occur in nature, the mixed layer clays have received most attention because of their compositional as well as stacking variability, and because of their geologic importance. These clay minerals occur almost exclusively in unconsolidated sediments and in relatively young sedimentary rocks.

The entropy of mixing of the layers, ΔS_m , is a small but positive quantity for the layers as such¹; its contribution to the free energy of mixing increases with rising temperature. The heat or energy of mixing may be either positive or negative, but is probably less sensitive to temperature (for the Ising model, this quantity is independent of temperature). Thus one ought to expect the effect of mixed layer formation to become more noticeable with rising temperature, contrary to the observed relations.

The answer lies, of course, in that in virtually all cases the formation of mixed-layer clay minerals involves layers having sheets of H₂O between the layers (montmorillonite, vermiculite). These sheets of quasi-crystalline H₂O molecules doubtless form "cushions" that smooth out the structural misfits between layers, and spread out the electric charges that originate in the interlayer cations. In entering the structure of the crystal, the H₂O molecules contribute to the free energy balance of the system, and a net decrease in the entropy of the enlarged system is expected because ΔS for H₂O, from the liquid to a quasi-crystalline state, should be large and negative, overshadowing other entropy effects. The total ΔS_m must be large and negative, so that mixed-layer formation should be favored by low temperature. Moreover, isothermally and isobarically the reaction should be sensitive to the value of the activity of H₂O in the surroundings of the crystal (for the description and interpretation of an analogous system involving the polypeptides in mixed organic solvents, see Davidson, 1962, p. 385-393), provided that H₂O behaves as a boundary value component (Zen, 1963, p. 930), as seems reasonable, especially if there is a circulating groundwater phase bathing the crystal. The disappearance of a mixed-layer clay mineral upon diagenesis of sediments and sedimentary rocks, thus, may be one of the earlier and more sensitive indicators of their "metamorphic" grade.

¹ One mole of layers of A and B in equal proportions will yield an ideal value of $\Delta S_m = R \ln 2 \approx +1.4$ cal/°K; however, a mole of layers represents an enormous quantity of matter. The dimensions of the crystal normal to the chain length do not enter consideration as long as the composition and atomic positions within each layer are held invariant when the stacking sequence is shuffled.

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