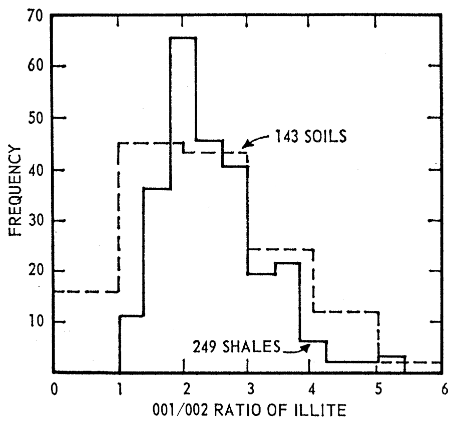

Fig. 4. Frequency distributions of (001)/(002) intensity ratio of illites for 249 shale and 143 soil clay fractions.

oclinic disordered structure) contracted layers. In mixed-layer illite-montmorillonites the potassium commonly occurs in the contracted layers and the K_2O content of these layers usually is in the ranges of 8 to 10 percent.

An excellent example of this is the mixed-layer illite-montmorillonite (4 : 1 to 3 : 1) (*6*) containing 7.39 percent K_2O. If all of it is in the contracted 10-Å layers (75 percent), as leaching tests indicate, these layers would contain 9.85 percent K_2O. The structural formula for this mixed-layer clay is:

$$\mathrm{K_{0.64}\ Ca/2_{0.10}\ Na_{0.02}}$$
$$\mathrm{(Al_{1.64}Mg_{0.36})\ (Al_{0.45}Si_{3.55})\ O_{10}(OH)_2}$$

If (i) the 75 percent 10-Å layers are illite-like and contain all the tetrahedral aluminum and the potassium and (ii) 25 percent of the layers are montmorillonites, have no tetrahedral aluminum, and contain all the calcium and sodium in the exchange position, the following two formulas can be calculated from the chemical analysis.

$$\mathrm{K_{0.84}}$$
$$\mathrm{(Al_{1.67}Mg_{0.32})\ (Al_{0.60}Si_{3.40})\ O_{10}(OH)_2}$$

Illite

$$\mathrm{Ca/2_{0.38}\ Na_{0.09}}$$
$$\mathrm{(Al_{1.54}Mg_{0.46})\ (Si_{4.00})\ O_{10}(OH)_2}$$

Montmorillonite

These structural formulas are almost perfect end members for high caliber illite and montmorillonite. If the entire base exchange capacity of 27 meq/100 g is assigned to the montmorillonite layers a value of 108 is obtained for these layers. These structural formulas must be reasonably close to the actual situation as a tetrahedral charge of this magnitude is almost essential for so much potassium to be strongly bonded. Likewise the expanded layers are not likely to have much of a tetrahedral charge as they will not contract when treated with potassium, and they will readily adsorb two layers of ethylene glycol.

Another interesting calculation of this type can be made. A structural formula for Wyoming bentonite is:

$$\mathrm{(Al_{1.64}\overset{3+}{Fe}_{0.15}\overset{2+}{Fe}_{0.02}Mg_{0.19})\ (Al_{0.10}Si_{3.90})\ O_{10}(OH)_2}$$

If all the tetrahedral aluminum is assumed to be concentrated in a few layers and if the tetrahedral portion of these layers are assumed to have the composition $(\mathrm{Al_{0.60}Si_{3.40}})$ then it can be calculated that the material contains 16.7 percent of these highly charged layers. Weaver (*7*) has reported that approximately 20 percent of the layers in this material have high enough charge to bond potassium and contract to 10 Å.

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28 October 1964

Crystal Packing of Molecules

Abstract. *The packing position of a molecule of known or assumed dimensions in a crystal can be found by minimizing the energy of the crystal with respect to molecular position by the method of steepest descent. Molecular flexibility can be introduced by allowing internal rotation about selected bonds. The method can be used to solve the diffraction phase problem in appropriate cases.*

If the shape of a molecule is known, or can be postulated from expected intramolecular distances and angles, the position of the molecule in a crystal unit cell of known dimensions and symmetry should be calculable. The molecule will position itself so as to minimize the free energy of the crystal. For practical calculations at constant entropy and volume, the potential energy of the crystal, E, may be minimized by positioning the molecule, subject to the constraints of the known lattice constants and cell symmetry, so that the sum of all nonbonded potential energies is a minimum. If an individual interatomic potential energy between atom j and atom k is E_{jk} then

$$E = \tfrac{1}{2} \sum E_{jk}$$

where the sum includes all the neighbors of a given molecule. Simple additivity of isotropic atom-pair interactions in the crystal is assumed. Temperature effects and zero-point quantum effects are neglected.

A computer program (*1*) has been written which minimizes E by a "steepest descent" procedure. The adjustable parameters are three translational parameters specifying the coordinates of the center of the molecule, three rotational parameters specifying the angular orientation of the molecule, and the six or less lattice constants. In addition, the program provides for flexibility of the molecule by allowing intramolecular rotations (subrotations) about selected bonds within the molecule. The program obtains the derivatives of E, with respect to the parameters, numerically. The derivative of E with respect to a particular parameter is obtained by increasing that parameter and reevaluating E; the derivative is the difference in E divided by the increment to the parameter. The gradient of E is thus obtained, and shifts are made along the gradient to minimize E.

Before any reliable calculations of positions of molecular packing could be made, it was necessary to have reasonably accurate interatomic potential functions (*2*); the Buckingham potential function was used:

$$E_{jk} = -A d_{jk}^{-6} + B \exp(-d_{jk}/\rho)$$

Considerable range for the parameters A, B, and ρ has been reported for the needed C—C, C—H, and H—H potential functions (*3*).

The potential parameters given by Kitaigorodskii (*4*) were tried first, having been developed for a similar purpose, but Bartell's potential parameters (*5*), developed primarily for intramolecular use, proved more satisfactory. Bartell's functions (approximated in Buckingham form) were used in our numerical work. There is considerable need for more accurate interatomic nonbonded potential functions. The packing program itself can be used to select the most appropriate potential functions, which are such that, when they are used in the program, known crystal structures are accurately reproduced; in other words, the calculated gradient should be zero for the observed structure when the correct potentials are used.

To prevent excessive length in the calculation, the summation was terminated when the interatomic distance under consideration was more than a certain distance (usually 2 Å) beyond the minimum in the potential function. This cutoff was found to be important in regard to its effect on the magnitude of the packing energy. On the other hand, preliminary results indicated that the calculated packing position was not greatly affected by the error caused by series termination.

The packing method has proved useful in solving the crystallographic phase problem. The calculated packing position of the molecule can be found with sufficient accuracy to permit routine refinement of diffraction data by least squares based on structure factor, starting with the calculated packing model. The previously unknown crystal structure of dibenzoylmethane ($C_{15}H_{12}O_2$) has been solved by a preliminary packing procedure based on least squares (*6*). In this structure the molecule is in a general position; thus three rotational and three translational parameters were determined for the molecule. The molecular position found by the packing program was then refined with x-ray diffraction data. The success of the packing method led us to devise the improved steepest-descent packing program described here.

This program was tested by application to several known crystal structures of aromatic hydrocarbons. The x-ray diffraction structures of naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) have been determined by Cruickshank (*7*) and Mason (*8*). Since the molecule has a center of symmetry, only three angles required determination. For naphthalene, the carbon positions in the calculated packing structure differed by a mean of 0.04 Å from the observed positions, with a maximum deviation of 0.08 Å; corresponding figures for anthracene were 0.08 and 0.11 Å.

The x-ray diffraction structure of phenanthrene ($C_{14}H_{10}$) has been obtained by Trotter (*9*). The molecule is in a general position, but, since the space group is polar, there are only two translational parameters in addition to the three angular parameters. The carbon positions in the calculated packing structure differed by a mean of 0.08 Å from the observed positions, with a maximum deviation of 0.13 Å.

The x-ray diffraction structure of 1,3,5-triphenylbenzene ($C_{24}H_{18}$) has been determined by Farag (*10*); the space group is again polar. Three subrotation parameters specify the rotations of the three peripheral phenyl groups, making a total of eight parameters to be adjusted. The initial packing model was assumed to be completely planar, with the *ortho* hydrogens bent back 20 deg. The packing program obtained phenyl subrotation angles of +39, −31, and +35 deg. The observed angles are +34, −27, and +24 deg, all ±2 deg. A possible explanation of the larger magnitudes of the phenyl subrotation angles found by the packing program is that no subrotation potential was used. The internal molecular energy increases as the phenyl rotation angle increases (*11*). Although such a potential parameter could have been included in the calculation, we believe that the present accuracy of the nonbonded interatomic potentials is not sufficient to refine such a parameter. The carbon positions in the calculated packing structure differed by a mean of 0.26 Å from the observed positions, with a maximum deviation of 0.56 Å. Although this agreement is not as good as those in the other tests, we believe that this is close enough to allow refinement of diffraction data by rigid body structure factor least squares.

Convergence was fairly rapid for the naphthalene, anthracene, and phenanthrene structures but slow for the 1,3,5-triphenylbenzene structure, in which case the summation limit was 1.5 Å. Experience with unknown packing structures is required for further study of convergence behavior. The usual requirement for the trial packing model, that the molecules do not penetrate each other, can be easily met by simple geometrical considerations.

Stronger intermolecular attractions, such as hydrogen bonding, may be handled by the program, provided reliable potential functions are available.

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Constant Volume, Self-Filling Nanoliter Pipette: Construction and Calibration

Abstract. *Pipettes with volumes ranging from less than one nanoliter to 200 nanoliters can be constructed by means of a simple mechanical system and calibrated by radioisotope and fluorescence techniques. Biological fluids can be transferred with a repeatability of 1 percent by this self-filling pipette of constant volume.*

Nanoliter quantities of biological fluids can be delivered conveniently and precisely by means of a constant-volume pipette consisting of a short length of small-bore quartz tubing sealed by fusion into a long piece of soft-glass support-tubing of larger bore. When the tip of the pipette is introduced into fluid, the length of quartz tubing fills automatically and completely by capillary action. Application of positive pressure by means of a syringe delivers a known volume of fluid with a high degree of precision. This volume can be calculated from the length and inside diameter of the quartz tubing. Calibration of the volume delivered may be accomplished by either radioactive or fluorescence techniques.

Nanoliter quantities of biological fluids are obtained during studies of microscopic regions of biological organisms. These fluids are usually subjected to several kinds of analyses which require the same volume of fluid for each determination. For these and other microchemical methods it is often necessary to add diluent and other reagents to the nanoliter samples. The accuracy of the results obtained depends on the precision with which such volumes can be transferred. To meet the requirements of several microchemical methods currently in use in our laboratory, we have devised a system for the construction of pipettes with volumes ranging from less than one nanoliter to 200 nanoliters, and reproducibilities of 1 percent.