Electrochemistry

Ernest Yeager and Robert A. Osteryoung will serve as *chairman* and *vice chairman*, respectively.

31 January. Henry Eyring; John O'M. Bockris; Michel Boudart, "Electrochemical catalysis."

1 February. N. S. Hush; R. A. Marcus; D. B. Matthews, "Quantum mechanical aspects of electrode processes."

2 February. Fritz G. Will; S. Schuldiner; Fred Anson, "Platinum"; speakers to be announced, "Special methods in electrochemistry" (for example, optical, thin layer, nonconventional relaxation techniques, strain electrochemistry).

3 February. Frank J. Morin; M. Fleischmann; B. E. Conway; Paul C. Milner, "The electrochemistry of oxides."

4 February. Robert Visco; Donald Maricle, "Electrochemical luminescence."

Santa Barbara Biltmore Hotel

Chemistry of Aging

Steven M. Horvath will serve as *chairman*.

24 January. Al Knutson; William Gillchriest; Denham Harman; Sam Lesher, "Molecular biology of aging—genetic regulation."

25 January. Ralph Brauer; F. Verzar, "Physiological parameters of aging"; Charles Barrows, "Chemical parameters of aging."

26 January. Albert Dorfman; George Stidworthy, "Chemistry of mucopolysaccharides", F. F. La Bella; Karl Piez, "Chemistry of collagen."

27 January. Effects of environmental stress on aging, I—Influence of pharmaceutical agents: A. D. Bender, "Mammalian systems"; Alan K. Done, "Developmental pharmacology"; Sheldon Aaronson, "Microbiological systems."

28 January. Stanley Mohler, "Reversal of certain undesirable features of the aging process"; Robert McGandy, "Nutrition, disease and aging."

Formulation of Research Policies

Lawrence W. Bass and Bruce S. Old will serve as *chairman* and *vice chairman*, respectively.

31 January, 1 February. Louis Henry; F. T. Rosser; Th. Franck; F. Goerlich; M. J. Cranley; Robert Major; Frederick C. Seitz, "Research policies at the national level."

2 February. A. A. Afifi; Stevan Dedijer; Alexander King; Arnold Kramish; F. N. Woodward, "Research policies in international perspective."

3 February. A. E. Pannenborg; Pierre Piganiol; speaker to be announced, "Corporate research policies."

4 February. Harry Melville; William J. Price, "Other major areas of policy."

This program is supported in part by a grant from the Air Force Office of Scientific Research.

W. George Parks
University of Rhode Island, Kingston

Rock-Forming Silicates

In recent years petrologists and mineralogists have found that the information presently available on the crystal structures of rock-forming silicate minerals is inadequate to solve many fundamental problems in the earth sciences. Such information is particularly important in three areas: (i) lattice energies and relative stabilities of different silicate structures; (ii) order-disorder relationships in silicates, especially those involving accurate knowledge of atomic distributions; and (iii) mechanisms of phase transformations and exact characterization of the phases involved. To bring together leading scientists from the various disciplines that bear on these problems, a conference on the crystal structures and crystal chemistry of rock-forming silicates was held at Lake Vermilion, Minnesota, 12–17 September 1965. The conference was attended by 50 invited participants from Australia, Canada, Germany, Iran, Japan, Switzerland, Turkey, the United Kingdom, and the United States. These scientists represented the fields of mineralogy, petrology, crystallography, physics, and chemistry.

The first session, dealing with polymorphism and phase transformations, was introduced by M. J. Buerger (Massachusetts Institute of Technology), Honorary Chairman of the Conference. He discussed the qualitative relations between changes in internal energy and changes in bonding, as reflected in the observable parameters of primary and secondary coordination. He pointed out that in phases related by displacive transformations the symmetry of the low-temperature form is always a subgroup of that of the high-temperature form. There are, also, a number of discontinuous transformation mechanisms in which some symmetry may be preserved, especially shear or shear-plus-differential dilatation. The higher symmetry often observed in the high-temperature forms may be based on the fact that the most symmetrical vibration modes of coordination groups are also those having the highest frequency. During the discussion T. Hahn (Aachen) said that, although the primary coordinations in high-temperature phases are often smaller than in corresponding low-temperature phases, there are several examples where the reverse is true. J. B. Thompson, Jr. (Harvard University), pointed out that some crystallographers incorrectly equate reconstructive and displacive transformations with first- and second-order transformations, respectively. The former are strictly crystallographic terms, whereas the latter are based on thermodynamic definitions.

Problems of order, disorder, and domain structures were discussed by Helen Megaw (Cambridge University) in terms of "pseudosymmetric" structures—those having subcells differing only slightly from one another because of puckering or segregation of atoms accompanied by puckering. The close similarity between subcells leads to the possibility of mistakes in the puckering arrangement. One can distinguish between localized disorder, a random distribution of individual mistakes where effects are not felt very far outside the unit cell, and extended disorder, where perfect domains exist with mistakes localized at domain boundaries. In cases such as bytownite, antiphase domains can blur out or completely remove the reflections caused by differences between subcells. However, these differences are indicated on Fourier maps of the "average" structure. Antiphase-domain boundaries are regions of different energy likely to be occupied by guest atoms; such boundaries may stabilize macrocrystals of non-end-member compositions, whereas at the end-member the single domain may be most stable. Framework geometry is controlled directly by temperature through a thermal expansion mechanism; site occupancy has a secondary effect. J. Papike (U.S. Geological Survey) showed that ordering of aluminum and silicon in scapolites is consistent with the nonstability of Al-O-Al linkages, the so-called "aluminum avoidance rule." C. W. Burnham (Geophysical Laboratory) discussed the effects of disorder of aluminum and silicon on the apparent anisotropic and equivalent isotropic temperature factors of the atoms in the tetrahedral coordination group.

A session on structural variation and the thermodynamics of silicate solid solutions was introduced by J. B. Thompson, Jr., with a discussion of the thermodynamics of internal ordering of crystalline solids. For a model of two atomic species distributed among two crystallographically distinct sites, he derived relations between the free energy of mixing and the cation distribution for both symmetric and asymmetric regular solutions. If the temperature of crystallization and the internal cation distributions at that temperature are known, one can obtain values for the free energy of mixing and the excess heat of mixing. For example, there is a large positive heat of mixing for hypersthene from the metamorphic granulite facies. Internal ordering may contribute significantly to deviations from ideality, and intensive examination of Fe-Mg distributions in various ferromagnesian silicates is needed. D. R. Wones (U.S. Geological Survey) presented data on the free energy of mixing of solid solutions of biotite. He stated that this quantity is influenced by the oxidation state of iron and by substitution of other ions in the octahedral sites, as well as by internal ordering. E-an Zen (U.S. Geological Survey) applied the Ising model to interlayered sheet silicates and derived heat-of-mixing terms as a function of the length of an average run. He discussed the mixed-layer clay minerals in light of these results.

Current problems in the classification of alkali feldspars were reviewed by F. Laves (ETH, Zürich). He discussed the stability of the various phases and the structural nature of the transformations between them. A distinction was made between triclinic aluminum-silicon distributions and distributions which are crystallographically triclinic but topologically monoclinic. D. B. Stewart (U.S. Geological Survey) presented the results of a detailed study of changes in unit-cell parameters as a function of composition and "structural state." Compositional changes produced by alkali exchange apparently leave the framework intact; such changes are reversible. The study furnishes much significant information on the structural relationships of alkali feldspars of intermediate "structural state." Heated discussion of the meaning of the term "structural state" led to the conclusion that this term refers to a set of structural parameters not necessarily restricted to the distribution of aluminum and silicon. P. H. Ribbe (University of California, Los Angeles) gave preliminary results of a structural investigation of an orthoclase with an intermediate degree of Al-Si order. Laves reported on the "schiller effect" in labradorites; this effect is caused by diffraction of visible light by parallel domains, the domain spacing being related to the wavelength by Bragg's law. Ribbe obtained similar results.

Introducing a session on bonding theory in silicates, D. W. J. Cruickshank (University of Glasgow) discussed the appreciable overlap that exists between the valence orbitals of silicon and oxygen. Such overlap, plus the fact that Si-O bonds are of virtually constant length (within ±0.05 Å), suggests that the effective charges are less than ±1 electron. Cruickshank outlined a theory of π bonding for silicates, by analogy to that for sulfates and phosphates. His theory is based on the fact that the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of the central atom have the correct geometry for the formation of π bonds with the $2p$ orbitals of oxygen. Simple applications of the theory lead to π-bond orders that correlate well with the relatively large bond-length variations in sulfates and phosphates. Since in silicates the bond-length variations are smaller, Cruickshank suggested that one must allow for effects of bonds between oxygen and other cations and for large Si-O-Si angles. He gave some evidence of agreement with observed Si-O lengths but cautioned that it is by no means certain at this time that the $3d$ orbitals of silicon are indeed effective participants in bonding.

Considerable discussion developed around the observation that when Si-O-Si angles are large (that is, 160° or greater) the Si-O bond lengths are shorter than normal. It was suggested that the oxygen atoms in such cases might in fact be randomly distributed around the time- and space-average positions, hence that the true bond distances might be closer to normal. Evidence from thermal-ellipsoid analyses of such oxygen atoms is, however, inconclusive at present. Cruickshank pointed out that the high-angle configuration might result in increased π-bond order, since the more linear geometry would enhance the ability of the oxygen $2p$ orbitals to contribute to such bonding. G. V. Gibbs (Pennsylvania State University) and J. V. Smith (University of Chicago) presented crystal-chemical data on olivine that, they suggested, were remarkably consistent with the classical ionic view of silicate bonding. Calculations of the temperatures of melting of diopside, of dehydroxylation of muscovite, and of the α-β quartz transformation were presented by M. Slaughter (University of Missouri). He based his calculations on simple ionic models modified by first-order approximations for exchange energies.

S. W. Bailey (University of Wisconsin) reviewed recent progress in crystallographic studies of layer silicates. Points of special interest in these studies are: (i) octahedral cation ordering is common, but tetrahedral orderering is confirmed in only three cases; (ii) oversized tetrahedral sheets articulate with smaller octahedral sheets by tetrahedral tilting around vacant octahedra, undersized tetrahedral sheets articulate with the octahedral sheets by tilting plus octahedral contraction or by inversion of some tetrahedra; (iii) the amount and direction of tetrahedral rotation and tilt, length of T-O, M-O, and O-O bonds, sheet thickness, and relation of cell dimensions to composition can now be predicted with some confidence. F. Liebau (Max-Planck Institut, Würzburg) discussed a series of anhydrous layer-silicate structures having the formula $A_m(Si_2O_5)_n$. He showed that the sheets are corrugated and the amount of corrugation is related to the size of the interlayer cation—the most corrugation being associated with the small cations. J. Zussman (Oxford University) described three recently determined layer-silicate structures—astrophyllite, lizardite, and zussmanite. M. Ross (U.S. Geological Survey) discussed mica polytypism and gave the method whereby the stacking sequence, crystallographic data, and intensity distribution of any particular polytype may be generated. Y. Takéuchi (Tokyo University) presented a possible mechanism by which polytypism in the dioctahedral micas may be explained.

Zussman reviewed the present state of crystal-chemical knowledge of pyroxenes and amphiboles. Although the fundamental structural models of both silicate classes are well known, the distinctions and variations between subclasses are not, because there have been few three-dimensional structural analyses of minerals in these groups. The distribution of iron and magnesium has been studied in only two cases, cummingtonite and hypersthene. Knowledge of alkali and calcium distributions and of the limits of solid solution between alkali and calcic amphiboles is completely lacking. It was also pointed out that complete understanding of the complex polymorphism of enstatite will be achieved only by x-ray studies of these phases at high temperature. The discussion of amphibole structures was primarily concerned with the distribution of cations other than silicon over the four available sites. C. T. Prewitt (Dupont Company) presented evidence that the tetrahedral sites as well as the A site may have to be considered as possible locations for these cations in certain amphiboles.

The problem of distribution of cations of varying size and its possible influence on silicate chain configuration in pyroxenes and the related pyroxenoids was the focus of much discussion. Joan Clark (U.S. Geological Survey) considered the lower-than-normal symmetry of omphacite and the possible existence of "domain" structures with regions having different cation distributions and possibly different space groups. Burnham suggested a likely pyroxenoid-type structure for a triclinic polymorph of ferrosilite, by analogy with pyroxmangite and rhodonite. D. A. Stephenson (University of Chicago) gave some results of high-temperature x-ray studies of enstatite by which a displacive transformation of clinoenstatite to a triclinic form has been discovered. Smith emphasized the necessity of studying structures at the temperatures where the crystals form, for the structures of the quenched products may be quite different. Liebau, in considering an extension of the concept of building chains, sheets, and frameworks from single and double tetrahedral units, pointed out that when certain cations not usually found in geologic environments are available, silicate structures containing chains built up from triple, quadruple, even quintuple tetrahedral units may be formed.

W. M. Meier (Technikum, Winterthur) developed an elegant classification of zeolites based on the simplest polytetrahedral building blocks from which the entire structure can be generated. In a comprehensive review he discussed the nature of exchangeable cation sites and the role of aluminum in these structures. There is evidence that alumina tetrahedra may be replaced by $(OH)_4$ tetrahedra under certain conditions. The distinction between feldspathoids and zeolites was found to be unjustifiable on structural grounds, for the various types of zeolite structures are at least as different from one another as they are from the feldspathoids. Discussion centered on the extreme difficulty of determining the positions of the exchangeable cations since most sites are only partially occupied. It was estimated that there are at least forty known zeolites whose structures have not been determined.

K. Fischer (Saarbrücken) introduced the closing session, on refinement of silicate structures. He discussed the importance of proper background measurement when using counter techniques and pointed out the severe criteria that must be satisfied by monochromators if they are to be used effectively. With respect to refinement results, he emphasized the importance of selecting an appropriate weighting scheme and the influence of anomalous dispersion and absorption corrections on thermal models. Finally, he demonstrated that by judicious selection of refinement procedures it is possible to determine Si-Al atomic distributions in disordered sites by the least-squares technique.

The problem of weighting appeared during discussion to be the least understood; Cruickshank aided considerably by citing the several criteria that must be met by a "correct" weighting scheme. Additional discussion focused on the problem of structure refinement in space groups of lower-than-apparent symmetry—for example, testing an ostensibly centric structure in the corresponding noncentric space group. The problems encountered in such a procedure were well documented. It was suggested that significance tests of the standard crystallographic R factor could indicate the validity of such refinements. The final discussion dealt with presentation of atomic thermal parameters and the question of the most appropriate procedure for correcting bond distances and angles for the effects of thermal motion. It was reemphasized that thermal data should be presented in terms of physically meaningful quantities, such as the magnitude and orientation of thermal ellipsoids, in addition to the anisotropic temperature-factor tensors.

Among the most significant results of the conference were the numerous possibilities for new directions and emphasis in silicate research indicated by the interaction of petrologic, chemical, and crystallographic approaches. Such stimulating interdisciplinary exchanges are possible only in small meetings such as this, and it is to be hoped that the success of the conference will lead to future meetings of a similar nature.

The conference was organized by a committee consisting of C. W. Burnham (Geophysical Laboratory), C. T. Prewitt (E. I. du Pont de Nemours and Co.), M. Ross and D. E. Appleman (U.S. Geological Survey), and T. Zoltai, director (University of Minnesota). It was sponsored by the Department of Geology and Geophysics, University of Minnesota, and was supported by a grant from the National Science Foundation.

TIBOR ZOLTAI
Department of Geology and Geophysics, University of Minnesota, Minneapolis

Calorimetry

Techniques and achievements in the field of calorimetry were the main topics of discussion at the 20th Calorimetry Conference, held in Ames, Iowa, 11–13 August 1965. Participants came from all sections of the United States and many foreign countries.

This year's meeting honored Daniel R. Stull (Dow Chemical Company) as its choice for the Huffman memorial lecture. Hugh Huffman, important for his research on the thermodynamic properties of amino acids, was the chief organizer of these conferences until the time of his death in 1950. At that time Stull assumed the responsibility.

The subject of Stull's address was the evaluation of thermodynamic data and the preparation of authoritative tables of properties. For many species of interest "one or more of the necessary facts are imperfectly known or even completely unknown." Preparing