Report on Research
Supported by Rockefeller Fund, July 1, 1932 - July 1, 1933.

During the year 1932-3 I have been assisted in researches carried on with the aid of the Rockefeller Fund by eleven men, of whom four were on whole-time or half-time appointment (Dr J.H. Sturdivant, Dr G.W. Wheland, Dr J. Sherman, and Dr. S. Weinbaum) and seven were not (Dr H.P. Klug, Dr E. Neuman, Dr E.B. Wilson Jr, Dr L.O. Brockway, Dr R. Hultgren, Mr B.N. Dickinson, and Mr _ Medlin). An account of the work is given in the following pages. Signed, L.P.

to Research Fellowships or Assistantships supported by this Fund

The general problem under investigation is the experimental determination of the structure of molecules and crystals in terms of atoms and ions or electrons and nuclei, and the development of structural theories correlating and extending the results of experimental investigation. Because of its extent, this problem is broken up into a large number of smaller investigations, dealing with one chemical substance or a group of related substances, or with one type of structure. Since July 1, 1932 we have attacked thirty or more such problems, and have carried about twenty-five investigations to completion. Papers communicating the results of twenty of these will have been published by August 1, 1933; their titles are listed at the end of this report. Of these papers, ten are mainly theoretical in nature, and ten experimental, indicating the essential equality of the emphasis placed on theoretical and experimental work in our program.

The experimental investigations involve mainly the determination of the structure of crystals by x-ray diffraction methods and the study of gas molecules by the diffraction of electron waves. In addition measurements of magnetic susceptibility, heat capacity, transition points, etc are made. The

theoretical work consists in the rigorous ~~solution~~ or approximate solution of the Schrödinger wave equation for simple atoms and molecules, the approximate quantum-mechanical treatment of complex molecules, the formulation of empirical rules compatible with quantum-mechanical ideas by the analysis of experimental data, etc.

The discussion of the researches may be given in several parts, corresponding to different classes of substances; namely,

1. Ionic molecules and crystals, including the silicate minerals.
2. The sulfide minerals and other inorganic crystals containing covalent bonds.
3. Organic molecules and crystals. The covalent bond in general.
4. Substances containing the three-electron bond.

1. Ionic molecules and Crystals.

The study of the structure of ionic molecules and crystals has ~~been brought~~ led during the last five or six years to the formulation of generally-accepted sets of ionic radii and of empirical rules regarding the stability of different structures, so that it can be considered that the principal problems in this field of investigation have been solved. ~~Further~~ Even such a ~~formerly~~ difficult and complicated subject as the structure of the silicate minerals has been completely clarified by this work. There remain however, a number of interesting ~~and~~ minor problems, some of which have been treated during the last year. The relation between ionic radii and ~~formulas~~ structure for oxygen acids has been discussed, leading to the ~~dis~~ recognition of the correct formula $HSb(OH)_6$ of antimonic acid (1). Dr Sherman, who had

previously ~~published~~ written a detailed account of Madelung constants and the calculation of crystal energies, has published a note on the Madelung constant of cuprite (2). Mr M D Shappell has discussed the cleavage of ionic minerals in relation to crystal structure. Dr Brockway and Professor Pauling have investigated the substances SF_6, SeF_6, and TeF_6 by electron diffraction, the molecules being found to be octahedral, with interatomic distances in good agreement with those predicted from ionic radii (3). PF_5 has been found to have the configuration of a square pyramid of F atoms, with the P atom nearly in the basal plane. Crystal structure investigations of zunyite, $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$ (4), $RbNO_3$ (5), NH_4HF_2 (6), and $Na_7(PO_4)_2F \cdot 19H_2O$ (7) have been carried out. Dr Hultgren has found from powder photographs that NH_4VO_3 does not have the perowskite structure. Investigations are at present under way on Mg_3TeO_6, $(NH_4)_2H_3IO_6$, $Al(PO_3)_3$, $CsAlSi_2O_6$, and other crystals.

2. The Sulfide Minerals and Other Inorganic Crystals.

The ~~structure of the~~ structural nature of the large group of sulfide minerals, which includes ~~many~~ most of the heavy-metal ore minerals and is in consequence of great practical importance, is not yet understood. Despite attack on the problem by a number of investigators, only a few sulfide crystal structures have been worked out. During the last year Professor Pauling and Dr M L Huggins have completed the formulation of tables of atomic radii for use in crystals and molecules containing covalent bonds. With these tables and of the recently-developed theories of the covalent bond, in conjunction with experimental investiga-

as part of our program.

tions, it is hoped that the structural principles underlying the sulfide minerals will soon be discovered. With this end in view, a number of crystal structure investigations have been carried out. The correct structures of chalcopyrite, $CuFeS_2$ (8), and sulvanite, Cu_3VS_4 (9), have been published. For both of these minerals incorrect structures had been reported by previous investigators. ~~a fact which illustrates the difficulties of these stu~~ The structure of sulvanite is particularly interesting, inasmuch as it differs in a remarkable way from the sphalerite structure. Dr Hultgren has shown from powder photographs that germanite has a sphalerite-type structure rather than the sulvanite structure. Enargite, Cu_3AsS_4, has been found to have a wurtzite-like structure, and binnite, Cu_3AsS_3, to have the same structure as tetrahedrite.

Other inorganic crystals containing covalent bonds whose structures have been determined or are under investigation are K_2SeBr_6 (10), by Dr Hoard and Mr Dickinson, KSCN (11), by Dr Klug, $Pd(NH_3)_4Cl_2 \cdot H_2O$, by Mr Dickinson, rhombic sulfur and monoclinic selenium, by Dr Klug, and CaB_6, by Professor Pauling. Dr Hultgren has also been studying the system Cu-Ru by X-ray methods.

3. Organic Molecules and Crystals. The Covalent Bond.

As a preliminary step to the discussion of the structure of molecules, Dr Wilson has been solving the Schrödinger wave equation for light atoms. After a study of the helium problem, he has found a reasonably accurate wave function involving four parameters for normal lithium (12). The extension of this treatment to normal beryllium, however, has not been very successful, and he hopes to improve the treatment greatly by introducing the inter-electronic distances in the wave functions. Mr Dickinson has applied the Rosen treatment to the hydrogen molecule-ion (13) and Dr Weinbaum has discussed the normal hydrogen molecule, with especial reference to the contribution of ionic structures (14).

As a result of the discovery of a simple method of calculating matrix elements for various electronic structures of molecules (15), Professor Pauling, Dr Wheland, and Dr Sherman have made great strides in the application of quantum mechanics to organic chemistry. The discussion of benzene and naphthalene has led to a quantitative knowledge of the contribution of various electronic structures to the normal states of these molecules, completely answering the old question as to the nature of aromatic nuclei (16). A similar treatment of hydrocarbon free radicals has provided an understanding not only of the general mechanism of stabilization of the radicals, through resonance of the odd electron among several positions, but also of the varying relative efficacy of different groups in producing stable radicals. An

analysis of empirical data on heats of combustion of organic substances has provided strong evidence that many molecules are resonating among several electronic structures, and has permitted the tabulation of resonance energies (17). The theoretical study of resonance in conjugated systems of double bonds and aromatic nuclei, including the dihydronaphthalenes and dihydroanthracenes, phenylethylene, stilbene, iso-stilbene, triphenylethylene, tetraphenylethylene, biphenyl, o, m, and p diphenylbenzene, and 1,3,5-triphenylbenzene, has led to an understanding of many properties of organic molecules, such as, for example, the relative ease of addition at different positions in naphthalene and anthracene. This work is now being extended to heterocyclic compounds, chromophore groups, etc.

On the experimental side, the determination of the atomic configuration and the deduction of the resonating electronic structures for methyl azide, cyanogen, diacetylene, and carbon suboxide have been carried out by ~~Professor Pauling and~~ Dr Brockway and Professor Pauling. Dr Klug is studying organic crystals by x-ray methods, including ortho-iodobenzoic acid (18), $C_2H_4I_2$, $C_2H_2I_2$, C_2I_2, etc.

4. The Three-electron Bond.

Since the discovery of the three-electron bond in 1931, a number of ~~[illegible]~~ molecules have been shown to contain it as an essential part of the electronic structure. The theoretical treatment of the simplest molecule in which this bond occurs, He_2^+, has led to a thorough understanding of its nature and properties (19). Electron-diffraction photographs made by Dr Brockway have shown the existence of this bond in ClO_2 (20). Moreover, the possibility that "potassium tetroxide, K_2O_4", might actually be KO_2, containing the ion $:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}:^-$, was investigated and verified by Dr Neuman by the determination of its magnetic susceptibility. Dr Neuman also found that potassium superoxide (as the substance may well be named) shows a transition at about 150° A., correspondingly probably to the transition of the $^2\Pi$ O_2^- ions to the lower of the two levels of the doublet. Dr Neuman ~~has~~ is also studying the crystal structure of this substance. Polarographic experiments on solutions of KO_2 in 6N KOH ~~which~~ kindly carried out by Professor Heyrovsky ~~support~~ indicate the ~~[illegible]~~ presence of the superoxide ion in solution and further indicate that ~~[illegible]~~ molecular oxygen and peroxide ions react to form superoxide ions.

Plans for 1933-4.

During the next year it is planned to continue research in the fields discussed above, with especial emphasis on applications to organic chemistry, ~~The attack on some organic problems will involve continued theoretical~~ with the hope that ultimately such problems ~~questions~~ as the structure of alkaloids, proteins, hemoglobin, etc. can be solved. In addition a number of investigations are planned to be carried out with the aid of the new ionization spectrometer, designed by Dr Sturdivant, which is now ~~nearly~~ completed and will soon be in operation.

Published Papers, 1932-3.

1. The Formulas of Antimonic Acid and the Antimonates. Linus Pauling, J.A.C.S. 55, 1895-1900 (1933).
2. Madelung constant Sherman Phil mag.
3. SF_6 etc Brockway + P Nat Acad
4. Zunyite P. Z Krist
5. $RbNO_3$ P. + Sherman ZK
6. NH_4HF_2 P ZK
7. $Na_7(PO_4)_2 \cdot F \cdot 19H_2O$ Neuman ZK
8. Chalcopyrite P + B. ZK
9. Sulvanite, P + Hultgren ZK
10. K_2SeBr_6, Koard + Dick. ZK
11. KSCN Klug ZK
12. Li Wilson J.C.P.
13. H_2^+ Dickinson JCP
14. H_2 Weinbaum JCP
15. Matrix elements P. JCP
16. Arom. sub. + Free Rad. P + Wheland JCP
17. Res. energies P + Sh. JCP.
18. O-iodobenzoic acid Klug JACS
19. He_2^+ P. J.C.P.
20. ClO_2 Brockway P.N.A.

Give titles etc as for 1.

Rockefeller Fund.

October 24, 1933.

Warren Weaver suggests sending in a request for extension of the fund immediately, action to be taken December 14th.

He says their policy is to support a definite biological program*. Atomic physics is definitely out. My work may be included because of its bearing on biological problems, though ordinary work in organic chemistry would not be.

In addition he has a small emergency fund which can be used for other problems. This is apportioned in December. I may come in under it.

* Especially quantitative work in biology