

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

311.05-11-3110260
311.05-11-3110560
311.05-11-3110561

January 31, 1968

NBS REPORT

9842

REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report
July 1 to December 31, 1967

The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Army Dental Corps; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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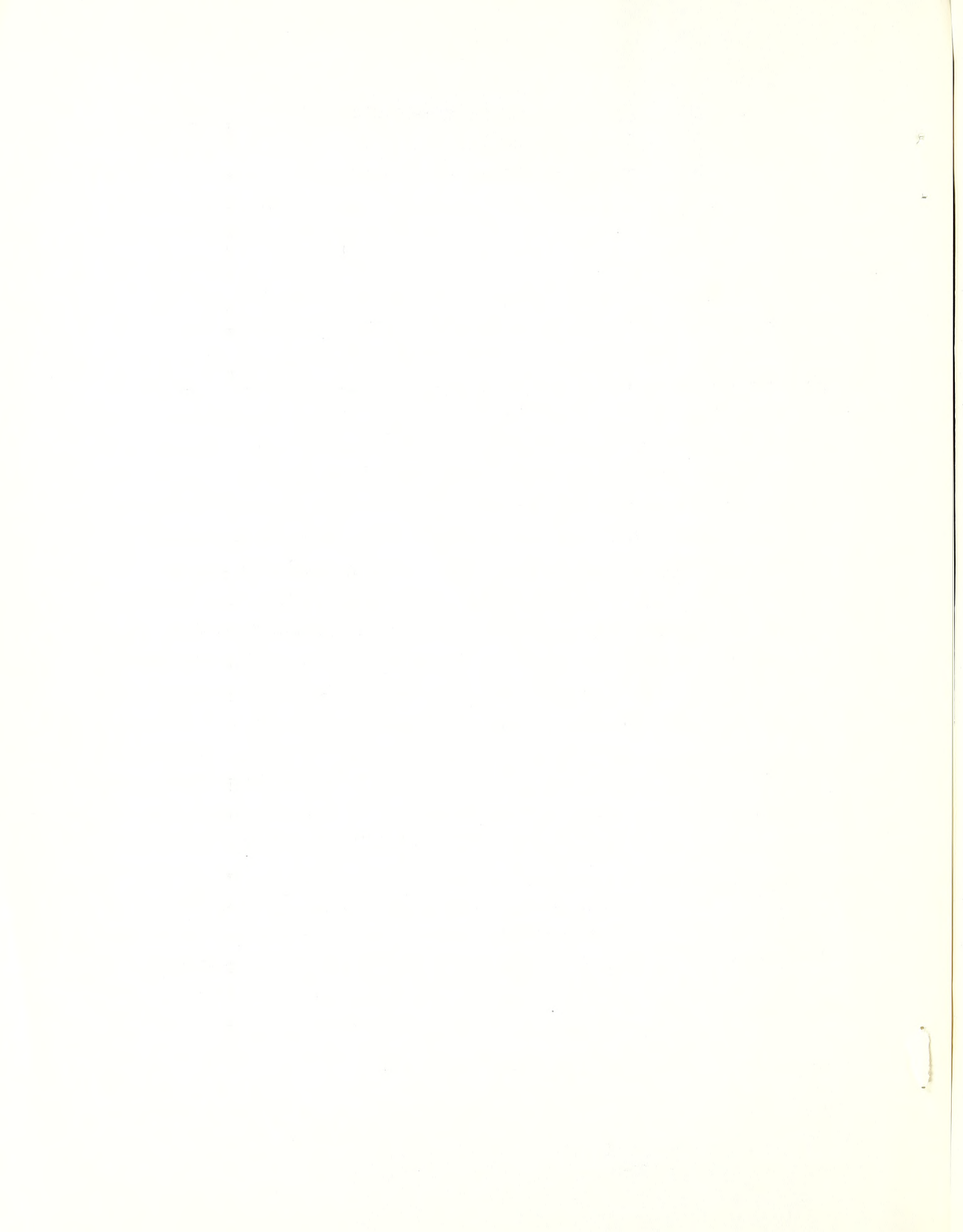
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NBS Report 9631	Preparation and Solubility of Hydroxy-apatite.
NBS Report 9650	Isothermal Diffusion in the Dilute Range of the System $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$. I - Theory.
NBS Report 9654	Calculations of Diffusion Coefficients in Ternary Systems from Diaphragm Cell Experiments.
NBS Report 9804	Aluminum Oxide as a Reinforcing Agent for Zinc Oxide-Eugenol-EBA Cements.
NBS Report 9820	The Reactivity of the Components of Tooth Structure.



REPORT ON DENTAL RESEARCH
at the
NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

This report covers dental research conducted at the National Bureau of Standards during the period July 1, 1967 through December 31, 1967 under the cooperative program sponsored by the American Dental Association; the National Institute of Dental Research; the U. S. Army Dental Corps; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration. In the summaries below of work in progress, sponsors of various projects are identified. However, since most of the projects are closely related both technically and administratively, all results are reported for the information of all sponsors. Detailed reports issued during the period on several phases of the work are listed below and are appended to this report.

2. REPORTS ISSUED

- NBS Report 9631 Preparation and Solubility of Hydroxyapatite.
- NBS Report 9650 Isothermal Diffusion in the Dilute Range of the System $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$.
I - Theory.
- NBS Report 9654 Calculations of Diffusion Coefficients in Ternary Systems from Diaphragm Cell Experiments.
- NBS Report 9304 Aluminum Oxide as a Reinforcing Agent for Zinc Oxide-Eugenol-EBA Cements.
- NBS Report 9320 The Reactivity of the Components of Tooth Structure.

3. PAPERS PUBLISHED

Pertinent Data on Some Physical Properties of Different Investments Used in the Casting of Gold Alloys. M. Ohashi, J. W. Stanford, and G. C. Paffenbarger. J. Nihon University School of Dentistry, 9:121, Sept. 1967.

Composition and Structure of Bone Mineral. W. E. Brown. Proceedings, First Conference on Biology of Hard Tissue, Princeton, 1965. N. Y. Acad. Sci. 1967, p. 46.

Ionization Constants of Substituted Benzoic Acids in Ethanol-Water. G. M. Brauer, George Durany, and Harold Argentar. J. Res. NBS (Phys. and Chem.) 71A:379, Sept.-Oct. 1967.

Analysis of Gold and Platinum Group Alloys by X-ray Emission with Corrections for Interelement Effects. J. D. Eick, H. J. Caul, D. L. Smith, and S. D. Raspberry. Applied Spectroscopy, 21:324, Sept.-Oct. 1967.

Diminishing Discoloration in Methacrylate Accelerator Systems. R. L. Bowen and H. Argentar. JADA 75:918, Oct. 1967.

Elastic Constants of Dental Amalgam. George Dickson and P. L. Oglesby. J. Dent. Res., 46:1475, Nov.-Dec. 1967.

4. WORK IN PROGRESS

4.1. Crystallography of Calcium Carbonates and Calcium Phosphates

Sponsor: NIDR, ADA

Crystal Structures: Work on the structures of various calcium carbonates and phosphates and related compounds is underway to provide background for understanding chemical reactions such as dissolution and crystallization and the incorporation of impurities in hard tissue. The objectives are described in greater detail in the preceding report.

$\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$: The structural analysis on this compound was successful and is complete except for cleanup of errors in the observed data, location of hydrogen atoms, and interpretation of the structure. An outstanding feature in the structure was the presence of Ca-CO_3 ion pairs surrounded by envelopes of water molecules. This is probably the first reported instance of occurrence of this ion pair in a crystalline structure, and it gives evidence of the structure of the ion pair in aqueous solutions.

$\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ (gaylussite): Our interest in this calcium carbonate relates to the presence of water molecules (in analogy with $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) and because of the sodium ions

which are components, also, of serum.

The structure of this compound has also yielded to analysis. It has been refined to completion and the hydrogen atoms have been located. The structure determining forces seem to be the formation of $\text{CO}_3\text{-Ca-CO}_3$ ion triplets as the primary force with subsequent coordination of one oxygen of 4 different CO_3 groups to the Na ions as the secondary force. The rest of the cation environments is made up of water molecules.

$2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ (burkeite): It appears that carbonate substitutes for sulfate in the lattice of this crystal, making it an interesting analog to the proposed substitution of carbonate for phosphate in apatites. Single crystals of burkeite were grown from aqueous solution. Most of these did not extinguish under crossed nichols, but one which did was examined by x-ray diffraction. The superlattice reflections, reported by others, were smeared, indicating that the proposed substitution does occur, but that there was considerable disorder in the sulfate and carbonate sites. This disorder would make difficult precise location of the carbonate groups, and for this reason, new attempts will be made to grow ordered crystals.

$\text{Ca}_4\text{O}(\text{PO}_4)_2$ (tetracalcium phosphate): An earlier optical and single-crystal x-ray study on this salt revealed that it had a probable structural relationship to hydroxyapatite. In the same way that the relationship between octacalcium phosphate and hydroxyapatite explains much of the anomalous chemistry of apatites with Ca/P ratios less than $5/3$, tetracalcium phosphate may have bearing on those with ratios greater than $5/3$. The crystals were found to be monoclinic instead of orthorhombic, as had been reported previously. X-ray intensity data for use in a structure determination has been collected. Work on the structure is being continued.

$\text{H}_3\text{PO}_4 \cdot 1\frac{1}{2} \text{H}_2\text{O}$: The structure of this compound was determined in cooperation with Tennessee Valley Authority. A major interest in this structure relates to the positions of the hydrogen atoms. Most of these were located, and evidence was obtained that two of the hydrogens may be delocalized. A manuscript describing this work was completed during the project period.

Apatite Analogs: The unit cells and spacegroups of the following apatite analogs have been determined:

	a	c
$\text{Na}_2\text{La}_3 (\text{SiO}_4)_6 \text{F}_2$	9.72	7.16
$\text{Na}_2\text{Pr}_3 (\text{SiO}_4)_6 \text{F}_2$	9.58	7.05
$\text{Na}_2\text{Nd}_3 (\text{SiO}_4)_6 \text{F}_2$	9.51	7.02

The spacegroup determined from the X-ray data is either Pb_3 or Pb_3/m . The criterion of 1 formula weight per unit cell suggests that the true spacegroup is Pb_3 , where 2Na and 2La in the 2b position form a column which alternates Na and La to replace the column of Ca's formed in hydroxyapatite by the 4f position in spacegroup Pb_3/m . The fact that the $\text{La}^{3+} \dots \text{La}^{3+}$ electrostatic interaction is 3 times as destabilizing as the $\text{La}^{3+} \dots \text{Na}^+$ interaction suggests that the Na/La columns are ordered.

CaRe_2 : A fairly regularly shaped crystal for which the necessary X-ray absorption corrections can be made has been selected and aligned in a manner suitable for data collection. The unit cell is approximately $a = 9.24$, $c = 4.81\text{\AA}$. We are awaiting the completion of the X-ray absorption program for the Univac 1108 computer before starting data collection. The objective of this study is to establish the degree of ordering in this compound.

4.2. Solubilities of Calcium Phosphates

Sponsor: ADA, NIDR

Solubility of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$: Work at 5°C on this compound

was completed. The solubility isotherms in the ternary system, $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ are now known at four temperatures, 5°, 15°, 25°, and 37.5°C. This salt was selected for intensive study initially because previous work indicated that it was the most amenable to accurate solubility measurements. In this way it was possible to study with greater accuracy some of the interionic effects that occur in the solution phase. As a result it was possible, for the first time, to establish fairly accurate stability constants for the ion pairs $[\text{CaHPO}_4]$ and $[\text{CaH}_2\text{PO}_4]^+$ at the four temperatures listed above along with the solubility product constants. By collecting data at four temperatures, it was possible to evaluate enthalpies of dissolution and ion-pair formation. These constants are listed in Table 1:

Table 1

Thermodynamic functions for $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and formation constants for the ion pairs CaHPO_4° and $\text{Ca}(\text{H}_2\text{PO}_4)^+$

Temp. °C	$K_{sp} \times 10^7$	$\Delta F^\circ{}^a$ Kcal/mole	$\Delta H^\circ{}^a$ Kcal/mole	$\Delta S^\circ{}^a$ e.u.	(CaHPO_4°) K_x^*	$\text{Ca}(\text{H}_2\text{PO}_4)^+$ K_y^*
5.00	2.38	8.4 ₃	1.3	-26	398	9.0
15.00	2.53	3.7 ₀	0.5	-28	299	4.7
25.00	2.54	9.0 ₀	-0.3	-31	244	8.2
37.50	2.41	9.4 ₁	-1.4	-35	396	3.0

^a Standard values for dissolution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

The techniques employed in the study were described in a paper, "Solubility of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and Formation of Ion Pairs in the System $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ at 37.5°C", and a paper on the work at 5, 15 and 25°C is under preparation. As an important part of this work, we have developed a least-squares method for computer evaluation of the constants from experimental data. This method takes into account the experimental observables (Ca, P, and pH) with appropriate weighing of errors, and it calculates the constants or parameters subject

to minimization of three condition functions:

1. Electroneutrality
2. Variation in the solubility product
3. Variation from the theoretical value in the stoichiometric ratio, Ca/P, of dissolution

By treating the data rigorously in this way, and by designing the experiments in the way described elsewhere in this report, we feel that one achieves a maximum in the reliability of the derived results.

Solubility of $\text{Ca}_5\text{OH}(\text{PO}_4)_3$: The data on solubility of hydroxyapatite, $\text{Ca}_5\text{OH}(\text{PO}_4)_3$, in the ternary system was re-processed by the computer techniques described above. Its solubility product constant was found to vary depending on the history of the sample; this helps to explain some of the disagreement on this subject in literature reports. We believe that the solubility constant for the steam-heated sample, $K_{\text{HA}} = 3.8 \times 10^{-53}$, represents that of the most stable form of hydroxyapatite, and constitutes a thermodynamic frame of reference for this material.

A manuscript, "Preparation and Solubility of Hydroxyapatite", summarizing the work on hydroxyapatite is appended.

Solubility of CaHPO_4 : The determination of the solubility isotherms for CaHPO_4 in the ternary system at the temperatures 5, 15, 25 and 37°C was completed. The solubility products and ion-pair formation constants are listed in Table 2:

Table 2

Thermodynamic constants for CaHPO_4 and formation constants for the ion pairs CaHPO_4° and $\text{Ca}(\text{H}_2\text{PO}_4)^+$

Temp. °C	$K_{\text{sp}} \times 10^7$	ΔF° Kcal/mole	ΔH° Kcal/mole	ΔS° e.u.	(CaHPO_4°) K_x^*	$\text{Ca}(\text{H}_2\text{PO}_4)^+$ K_y^*
5.00	2.03	8.8 ₆	-4.1	-17	222	5.3
15.00	1.63	8.9 ₃	-4.1	-17	142	10.2
25.00	1.29	9.4 ₀	-4.1	-18	291	9.9
37.00	0.97	9.9 ₅	-4.1	-19	212	4.1

The ion-pair constants are in reasonably good agreement with those obtained with $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ given in Table 1.

Solubility of $\text{B-Ca}_3(\text{PO}_4)_2$ (whitlockite): In our solubility studies, we routinely calculate the ion-activity products of all the calcium phosphates of each solution for which we have analytical data. These calculations reveal that in many instances, whitlockite may be more insoluble than has been recognized. Since it is a component of calculus, it has obvious importance. As a result, we have estimated its solubility-product constant using cryogenic and thermal data, and we have initiated an experimental program to measure its solubility. Our preliminary results show that the solubility product for this compound, $(\text{Ca}^{++})^3(\text{PO}_4^{3-})^2$, is approximately 10^{-29} .

Stoichiometry of Whitlockite: The suggestion has been made that whitlockite has the formula $\text{Ca}_{10}\text{H}(\text{PO}_4)_7$ rather than the one usually given, $\text{Ca}_3(\text{PO}_4)_2$. The suggestion raises serious uncertainties concerning the thermodynamic properties and the nature of the solubility product for this material. Experiments are being carried out to test the Ca/P ratio of whitlockite by measuring the amount of pyrophosphate that is produced when acid calcium phosphates are heated. The initial results to date indicated that the composition of whitlockite is variable, at least in the temperature range of the experiments, 700 to 900°C, but more recent data do not confirm the initial results. Work on the stoichiometry of whitlockite is continuing.

Solubility of $\text{Ca}_3\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$: In our studies we have placed importance on this salt because of its relationship to hydroxyapatite and because it may participate in the formation of tooth and bone mineral. Our knowledge of the solubility of this salt is based on one point in the ternary system at 25°C. In view of its importance, this is an inadequate basis to predict its chemical behavior. We have

initiated a program to measure its solubility over a range of solution compositions and at other temperatures. Materials for the study are being prepared; the first series of solubility measurements proved to have an apparent unbalance in the electroneutrality of the solutions, and are to be repeated.

Diffusion in the ternary system $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$: It is not generally realized by workers in this field that diffusion in a ternary system is very complex, particularly when weak electrolytes such as H_3PO_4 are present. As a result, it is common practice to oversimplify treatment of experimental data by the use of Fick's law. Our work shows that this may lead to gross errors in the interpretation of kinetic measurements.

The cells previously used in our experimental studies introduced an extra complication in that surface diffusion occurred in the sintered glass diaphragm. A new cell using a millipore membrane was constructed which would obviate this particular problem. Experimental data are being collected using this cell.

Another result of this work has been the development of a novel method for the calculation of diffusion coefficients from experimental data from diaphragm cells. In the past, it has been necessary to carry out two experiments when three-component systems were being studied. The present method, which is an application of a generalized least-squares procedure, allows this to be done from a single experiment and without any restrictions on the initial conditions.

Two reports covering this work, "Calculation of Diffusion Coefficients in Ternary Systems from Diaphragm Cell Experiments" and "Isothermal Diffusion in the System $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$: I. Theory", are appended.

Theoretical Consideration of the Solubility of Apatites:

Solubility studies on hydroxyapatite have yielded discordant results which frequently have led the investigators to propose unusual explanations, some of which are inconsistent with thermodynamic theory, and others have no known parallels in other chemical systems. Therefore, the solubility problem was examined, starting from fundamentals. The following are some of the conclusions:

1. It is possible to introduce the "surface" as a phase without violating the basic principles that lead to Gibbs phase rule. The surface, as a phase, does not change the number of degrees of freedom normally associated with the system. This comes about because more information is needed to describe the composition of a surface than for any other phase.

2. The surface cannot restrict the composition to an isotherm nor will it lead to a valid solubility product constant, per se. It is only when the lattice phase is in equilibrium with the solution that solubility product principles can be applied. This is true even though the surface causes the stoichiometry of the overall dissolution reaction to be different from the stoichiometry of the solid.

3. The system, $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$, is normally considered to have three components. Actually it contains four constituents, and limiting it to three components is valid under a stoichiometric restriction which may not be applicable to nonstoichiometric hydroxyapatite.

4. It is shown through use of the Gibbs-Duhem equation that small variations in stoichiometry of the solid do not invalidate application of solubility product principles.

5. The charge on the surface of finely divided hydroxyapatite particles can be treated as a fourth component in the system, $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$.

6. Factors such as particle size, surface energy, nonstoichiometry, surface equilibrium, and surface phases make it mandatory to define carefully the model for the equilibrium and to use a thermodynamic treatment which is consistent with that model. Much of this difficulty arises from the sparingly soluble character of hydroxyapatite.

A manuscript describing this work is in preparation. Several of these points were verified in experimental studies described elsewhere in this report.

4.3. Adsorption Studies

Sponsor: NIDR

Surface Studies of HA: Earlier, reference was made to a theoretical treatment which distinguishes between "surface" and "lattice" reactions. Finely divided hydroxyapatite (surface area $25 \text{ m}^2/\text{g}$) was found to have a high capacity for calcium and phosphate ions through adsorption experiments. For example, on equilibrating a finely divided HA preparation with dilute H_3PO_4 solution, the final PO_4 concentration was less than the initial even though part of the solid had gone into solution as evidenced by an increase in calcium concentration. In spite of the adsorption of phosphate, it was found that the final equilibrium behavior could be explained on the basis of the solubility product for the lattice reaction, as anticipated from theory.

The results of surface exchange studies (described in previous reports), using Ca^{45} and P^{32} in hydroxyapatite-saturated solutions in the ternary system were used in a "compartmental" analysis. The results are consistent with the idea that three processes were occurring, one very rapid (and presumably reversible), a reversible reaction with intermediate rate, and a slow irreversible reaction. The isotopic dilution technique proved very useful for measuring

the second of these components. Evidence was found that the composition of the surface changes as the pH of the saturating solution is varied.

It was discovered that the earlier approach to the two-process problem of adsorption from solution was only an approximation whose degree of exactness was greatest when the degree of competition (of the two adsorption processes for the adsorbable species) was least appreciable. An exact solution for the problem was ultimately found which resorted to a numerical integration when it was learned that the system of differential equations could not be integrated in closed form. Application of the isotopic exchange measurements to the adsorption theory is the basis of a paper now in preparation. Determination of the six parameters involves a non-linear least square optimization procedure which utilizes two iterative processes alternately. The relative magnitude of certain of these parameters in the isotopic exchange of calcium and of phosphate sheds light upon the stoichiometry of the deposited crystals.

4.4. Reactivity of the Components of Tooth Structure

Sponsor: NIDR, USA, USAF

A restorative material capable of adhering to tooth structure is greatly needed. Bonding is complicated by the complex nature of tooth structure as well as the mechanical, toxicological and bacteriological conditions which occur in the oral cavity. Apparent heats of wetting (ΔH_w) measurements of dentin, enamel, and anorganic whole tooth tissue of known specific surface have been used to study the reactivity and degree of surface modification produced by various ions and functional groups in an aqueous environment employing the technique previously developed.

A decrease in the ΔH_w value of dentin in water from 4100

ergs/cm² to 1590 ergs/cm² in 2% to 40% aqueous solutions of organic solvents suggests the strengthening of electrostatic bonds between polar groups of the collagenous matrix of dentin. In absolute ethanol and hexane, dentin absorbs heat indicating the weakening of hydrophobic bonds. ΔH_w values for anorganic whole tooth in organic solvents (~ 34 ergs/cm²) are not appreciably different from those obtained in water (109 ergs/cm²). The presence of NO_3^- , NO_2^- , CNS^- , $\text{SO}_4^{=}$ and I^- , at pH 5 depressed the ΔH_w of dentin to 2,000 ergs/cm². Other anions (F^- and Cl^-) had no effect. At pH 8, however, anions did not alter the ΔH_w of dentin. The addition of aldehyde groups to the liquid adsorbate at pH 8, however, resulted in the lowering of the apparent ΔH_w of dentin. Significant changes in ΔH_w values for anorganic whole tooth were not observed in the presence of anions or aldehyde groups. Thus, the surface of dentin may be modified by pre-treatment with non-polar solvents. Ionic bonding to exposed polar groups can be achieved at the optimal pH. A progress report on this work is appended.

4.5. Characterization of Components of Tooth Structure and Dental Materials by Differential Thermal Analysis

Sponsor: NIDR

Differential thermal analysis has been extended up to 1150°C. The melting ranges of dental golds of Types I, II, III and IV were determined in an argon atmosphere. In all cases, well-defined endothermic peaks were observed for the gold component. On reheating, the peak temperature changed for some of the alloys indicating oxidation of the less noble alloy constituents. Although differences were observed between the peak temperatures obtained in the DTA measurements and the melting ranges determined from cooling curves, the DTA thermograms are very useful for characterizing dental gold alloys. The thermograms of components of tooth structure,

and hydroxyapatite, fluorapatite, octacalcium phosphate and tricalcium phosphate have been obtained. Presence of certain impurities such as carbonate in β -tricalcium phosphate can be detected from the thermograms.

4.6. Mechanical Behavior of Skin

Sponsor: NIDR

Using the model system of rat skin to gain insight into the mechanical behavior of the mucous membrane of the oral cavity, a study is being carried out on the thermodynamic and viscoelastic properties of rat skin under various mechanical conditions and at various temperatures. It was noted in the previous report that the mechanical behavior of rat skin in the 50°C range and above became thermodynamically controlled due to first order phase transition phenomena all or in part related to the collagen \rightarrow gelatin transition. For example, as previously reported, the transition was followed as a function of the force of contraction which began around 56°C and reached a maximum between 60 and 70°C, which is in general agreement with the shrinkage temperature for rat skin reported in the literature of 65°C due to the collagen \rightarrow gelatin transition.

During this period, a study has been made on the first order phase transition phenomena occurring in skin above 50°C using a differential calorimeter. A calorimeter has been developed which will determine the onset temperature, as well as measure quantitatively the magnitude of the first order phase changes occurring in skin from 50°C to 100°C. It has been shown that the onset of the first order phase transition in samples of back skin from a 493 gm rat occurred around 54°C irrespective of sample size as followed calorimetrically. However, if the sample was soaked in water, this onset appeared to be shifted to a lower temperature,

which is in agreement with the dilution effect on the collagen transition reported in the literature. This skin fluid content effect on the transition-phenomena needs further investigation.

It was further noted, using the back skin from a 493 gm rat, that when the total calories released between 54°C and 93°C due to first order transition phenomena were plotted against sample size, a linear plot was obtained. Thus, the total calories released per gram of back skin could be calculated and were found to be approximately 4.2 cal /gm as compared to that reported in the literature for pure collagen at 12.5 cal /gm. The value for back skin of a 493 gm rat may not only be due to the collagen - gelatin transition, but due as well to other protein transition since a plateau was observed with every sample size at around 63°C.

4.7. Mechanical Properties of Materials

Sponsor: NIDR, USAF

A torsion pendulum system has been developed for determination of elastic properties and internal friction of materials. The specimen serves as the torsion bar in the system. From the frequency of the system, the shear modulus of the specimen material can be determined and from the damping the internal friction can be measured. Shear modulus is determined using the equation $G = \frac{8\pi l M f^2}{r^4}$ where G is the shear modulus, l and r are the length and radius of the cylindrical specimen and M and f are the moment of inertia and frequency of the system. Since the maximum length to radius ratio that can be obtained with many dental materials is small, specimen end effects have a relatively large effect on the frequency of the system. Therefore, an effective length must be determined by making measurements with various specimen lengths. A value of 3×10^6 psi has been

obtained for the shear modulus of dental amalgam. This is in agreement with values obtained by ultrasonic methods. The torsion apparatus is applicable to many restorative materials and to natural tooth structure. Studies of the effects of temperature variations on the mechanical properties of tooth structure will be made with this apparatus

4.8. Stress Analysis

Sponsor: NIDR

In order that a more scientific approach can be implemented in the design of restorations, bridges and dentures, a study is being made on the way stresses are distributed in teeth under various loading conditions. The problem is extremely complex due to the fact that the structures are made up of several different materials, several of which are not homogeneous or isotropic.

To solve some of these complex problems, the assumption of plane stress has been utilized by several authors who constructed and analyzed thin photoelastic models. Besides the obvious discrepancies in this approach, such as the use of homogeneous, isotropic materials and the use of only one material to represent a structure which is composed of more than one material, the use of the assumption of plane stress is also questionable. To test its validity, a computer program which solves stress analysis problems for either a plane stress or an axisymmetric case was obtained. It was theorized that a cuspid could perhaps be more validly represented as an axisymmetric rather than plane stress structure. An idealized cuspid was then studied under an axial loading by the plane stress and axisymmetric structures approach. The results from the two studies were considerably different, so it was concluded that a simplifying assumption (such as plane stress or axisymmetric structure) was

not valid, and that a more exact three-dimensional approach should be used.

Consequently, work is currently under way to write a computer program which will determine the stresses in an arbitrarily shaped body subjected to an arbitrary loading. It is felt that this program, which will require almost a year to complete, will have general applications in stress analysis, and will be of particular help in the determination of stress distributions in periodontal structures.

4.9. Metallurgy

Sponsor: ADA, USAF, VA

Gallium Alloys. Our work on gallium alloys has now been completed and will be summarized in a published paper. During the past six months we have established that a delayed expansion does not occur in gallium-palladium-tin alloys which had been contaminated with a saline solution. However, an excessive initial setting expansion appears to result from such contamination. The same precautions must therefore be exercised to prevent contamination by moisture as when using zinc-containing amalgam alloys.

The elastic constants of several gallium-palladium-tin alloys were measured using ultrasonic methods. A Young's modulus value of $12.0 \pm 0.6 \times 10^6$ psi was obtained which may be compared to a value of $9.1 \pm 0.1 \times 10^6$ psi for dental amalgam. It is therefore concluded that the stiffness or rigidity of the gallium-palladium-tin alloys under rapid loading is significantly greater than the stiffness of dental amalgam.

A result of even greater significance for clinical use, however, is the recent finding that actual restorations of the gallium-palladium-tin alloy resist leakage at their margins to a significantly greater extent than is the case

with similar restorations of dental amalgam. In these studies, we used the method of Pickard and Gayford⁽¹⁾ in which air pressure is applied beneath the hardened restoration through a channel in the root canal of extracted teeth and the amount of pressure needed to produce leakage under water is measured. The gallium alloy restorations consistently resisted pressures up to 100 psi while amalgam restorations generally leaked at 20 to 60 psi.

Noble Metals. Studies of phase diagrams for noble-metal alloys are continuing. Alloys of unusually uniform composition and homogeneity have been prepared and analyzed quantitatively using an electron beam microprobe. Calibration of the microprobe has been completed for chromium-platinum alloys and subsequent work now in progress should reveal the location of phase boundaries directly. The nature of the order-disorder reactions in this alloy system are now being studied with a view toward possible hardening of these alloys by using a suitable heat-treatment.

(1) H. M. Pickard and J. J. Gayford, Brit. Dent. J., 119, 69 (1965).

4.10. Development of an Adhesive Dental Restorative Material

Sponsor: ADA, USAF, VA

The material under investigation can be divided into three parts: (1) a polymerizable liquid that is mixed with (2) a reinforcing filler, this mixture making up the bulk of the restorative material, and (3) adhesion-promoting primers that are applied to the tooth surface in the form of a very thin film.

With regard to the monomer system (the ternary eutectic system HEMA-isophthalate, HEMA-terephthalate and HEMA-phthalate that we discovered previously - these materials

are now commercially available) we have purchased a quantity sufficient for our continuing research. These monomers have been formulated with suitable stabilizers, accelerators and other additives under investigation, and a resultant formulation has been evaluated for systemic toxicity and local irritation. It was found to be non-toxic and non-irritating. One of the necessary additives to this monomer system is a tertiary aromatic amine that functions to accelerate the polymerization to give the desired three-minute hardening time. The materials previously available have contributed to discoloration of the filling and are in themselves somewhat toxic. New tertiary aromatic amine compounds were synthesized in an effort to reduce discoloration (by steric hindrance) and to decrease toxicity (by increasing the molecular weight of the compounds into the neighborhood of 300-500). Accordingly, the following amine accelerators were synthesized:

N-methyl,N-lauryl-p-toluidine

N-methyl,N-lauryl-sym-xylidine

N,N-dimethyl-p-laurylaniline

The first two compounds were synthesized by reacting lauryl bromide with the corresponding ring-substituted N,N-dimethylaniline. The last compound was prepared by methylating p-laurylaniline. Generally, the compounds were comparable in their ability to accelerate polymerization and in the color stabilities of the resulting composite materials. More definitive comparisons are currently being made. With regard to the reinforcing fillers for the restorative material, special glasses were developed. They contained barium to give X-ray opacity so that the fillings will contrast with decalcified (cariou) dentin in roentgenograms. Thus, the dentist will be able to detect recurrent decay. Attention was given to minimizing the thermal expansion coefficient

and to matching the refractive index with that of the matrix polymer.

With regard to the adhesion-promoting compounds, numerous candidate materials were synthesized. Only one of these mediated a significant improvement in the bond between the filling material and dentin, and this improvement was not as great as that produced by NPG-GMA (the adduct of N-phenylglycine and glycidyl methacrylate). Numerous formulations based on NPG-GMA were prepared and tested for their relative adhesion-promoting ability. Adhesion in the range of 700-800 pounds per square inch was obtained with the best of these. However, a number of these formulations were not stable, and they polymerized in their containers. Consequently, work has commenced with the objective of synthesizing improved stabilizers for the adhesion-promoting formulations. Independently, investigators in Tokyo reconfirmed the ability of NPG-GMA to promote adhesion to hard tooth tissues; it gave the highest adhesion values of a number of compounds which they have synthesized and tested.

Clinical Studies: Clinical investigations of these composite materials and other experimental materials are continuing. Since the toxicity tests were favorable and approval was given by the Committee of Institutional Associates of the American Dental Association, a formulation utilizing the ternary eutectic monomer systems has been used in clinical restorations. X-rays have been taken of these restorations, and it has been established that the barium concentration in the barium-glass reinforcing filler is at a suitable level for diagnostic purposes.

4.11. Zinc Oxide-Eugenol Materials

Sponsor: USA

Cements: Recent work in this laboratory has led to

greatly improved aluminum oxide reinforced zinc oxide-o-ethoxybenzoic acid (EBA)-eugenol crown and bridge cements. These products have become commercially available and have been well accepted by the dental profession. A report on studies to improve these cements is appended.

Restorative Materials: The objective of the present research is the development of a longer lasting temporary zinc oxide-EBA-eugenol restorative material that will yield sedation and protection of the tooth from irritants and decay. Formulations containing 64% ZnO, 30% Al₂O₃ and 6% hydrogenated rosin and 62.5% o-ethoxybenzoic acid (EBA) and 37.5% eugenol have excellent physical properties. Limited clinical studies have shown that the restoration does not dissolve in oral fluids and can be used for one or two surface restorations in non-functional areas. These cements do not hold up under extreme masticatory loads. To increase the resiliency of the hardened cement, resinous substances such as poly(methyl methacrylate) have recently been incorporated into the powder component. Further improvements have been obtained by employing a carbonate-containing zinc oxide and a bentonite coated non-caking rosin. With these components diametral tensile strength values as high as 1300 psi, as compared to 500 psi for other commercially available "improved" zinc oxide-eugenol restorative materials, have been obtained. It is believed that these products will last one to two years, resulting in great savings in the clinician's and patient's time.

4.12. Rapidly Fabricated Surgical Splint

Sponsor: USA

About 25% of all injuries incurred in combat are manifested as damage to facial structures. Among these, fractures of the mandible commonly occur. The presently employed

technics of splinting fractures of the mandible using arch-bars are not only traumatic to the oral tissues, but are also time-consuming and require highly trained personnel and specialized laboratory equipment and facilities.

A polymeric material suitable for the rapid fabrication of splint-type appliances for the fixation and stabilization of fractures of the mandible has been developed. This material consists of a very small particle size polymer powder (70% poly(methyl methacrylate) resin with 30% CaCO_3 and 0.2% benzoyl peroxide) and a monomer liquid (methyl methacrylate with 0.2% dimethyl paratoluidine). The dough-like product formed on the mixing of the powder and liquid can be readily adapted to the cervical third of the intact teeth. Auto-polymerization occurs in the mouth within 4-7 minutes at peak temperatures not exceeding 50°C . The polymerized product exhibits sufficient strength, rigidity, and dimensional stability to function as a splint. Preformed, spring-like lingually inserted clasps prevent the buccal displacement of the polymerized splint and serve also as anchor points for interarch elastics. The use of the "rapid splint" precludes the need for cast arch bars and complicated wiring procedures. Limited clinical tests that will supply a feedback for further modification, if necessary, will be conducted at Walter Reed Medical Center. The same polymeric materials may find application as a hard denture reliner and as orthopedic splints.

