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EFFECTS OF ULTRAHIGH PRESSURES ON THE
FORMATION AND PROPERTIES OF ORGANIC,
SEMIORGANIC, AND INORGANIC MATERIALS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-73, Pt. II
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Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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(Prepared under Contract No. AF 33(616)-7471 by
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FOREWORD

This report was prepared by Battelle Memorial Institute under AF Contract No. AF 33(616)-7471. This contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 73404, "Effects of Ultrahigh Pressures on the Formation and Properties of Organic, Semiorganic, and Inorganic Materials". This work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. Albert J. Sicree, Jr., acting as project engineer.

This report covers work performed during the period January, 1962, through December 31, 1962.

This work was conducted by E. J. Bradbury, H. H. Krause, C. B. Sclar, L. C. Carrison, G. F. Ward, C. R. Gray, R. C. Himes, C. M. Schwartz, and R. I. Leininger.

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ABSTRACT

It was found that superpressure alone could effect crosslinking of polybutadiene and apparent copolymerization of vinyl monomers to polybutadiene. In a somewhat similar fashion, methylmethacrylate was added to polymethylmethacrylate to give increased-molecular-weight products. The pressurization of other polymers such as polystyrene, polycaprolactam, and polymethylmethacrylate did not produce large changes. It was concluded that these pressures would not cause significant reforming of these polymer chains or reactions in the aromatic or carbonyl double bonds. Polymerization of quinone to a relatively heat-stable material was effected by pressurization.

Dimethyldicyanosilane has been converted to an insoluble polymeric material by pressurizing to 105,000 atmospheres at room temperature. Aluminosiloxanes having either acetylacetone or isopropoxide bonded to the aluminum, and methyl, ethyl, or phenyl groups on the silicon, have been polymerized further and probably crosslinked by a combination of pressure and heat. As pressure was increased, the Al-O-C bonding was stabilized, and the rupture of Si-C bonds was inhibited. Decomposition of an arsenosiloxane based on trivalent arsenic was promoted by pressure, while one based on pentavalent arsenic was stabilized. Formation of phthalocyanine polymers appeared to be inhibited as pressure was increased. Polymerization of aluminum phenoxide by pressurization resulted in the same products as were obtained by heating.

The equilibrium composition of stoichiometric and nonstoichiometric iron monosulfide was shown to be pressure-temperature dependent. A new high-pressure form of aluminum phosphate, probably $[Al_2(PO_4)_2 \cdot Al(OH)_3]$, was synthesized from hydrated aluminum phosphate and from the quartz form of $AlPO_4$ plus water. This new phase is stable to at least 110,000 atmospheres and 1300 C and is 18 per cent denser than the ambient-pressure quartz form of $AlPO_4$. It is harder than spinel and topaz and approaches the hardness of corundum ($\alpha-Al_2O_3$). An iron analogue of this high-pressure aluminum phosphate was synthesized from hydrated ferric phosphate. At pressures between 50,000 and 110,000 atmospheres, another new high-pressure form of iron phosphate was found. Zirconium pyrophosphate transforms to a new high-pressure polymorph between 45,000 and 105,000 atmospheres which is 15 per cent denser than the ambient pressure form.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

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I. INTRODUCTION

Battelle Memorial Institute has been studying the effects of ultrahigh pressures* on organic, semiorganic, and inorganic monomers and polymers for 2-1/2 years under the sponsorship of the Aeronautical Systems Division. This project was initiated by the Air force as part of its continuing search for new and improved materials. Such new materials are needed as manned and unmanned aircraft reach greater and greater speeds and higher and higher altitudes. Improved thermal and radiation resistance become essential.

During the first portion of this contract, described in Technical Documentary Report No. ASD-TDR-62-73, progress was made towards the determination of the effects of these ultrahigh pressures. Although equipment capable of producing the target pressures was available, modifications of the technique and sample capsules had to be made in order to work with the desired materials. This was especially necessary in the case of the highly compressible organic materials. Because the pressurized samples were quite small, some standard techniques had to be modified for use on a very small scale. Methods used for examination of the pressurized samples included microscopy, infrared spectroscopy, crystallography, X-ray diffraction, densitometry, viscometry, and differential thermal analysis. Using these methods, it was found that measurable changes were effected by these pressures in all of the classes of materials. In the case of organic polymers, changes induced in polymers were found to be quite small. More definite evidence of changes was found in the semiorganic materials, as for example, in the case of the dimethyl dicyanosilane. With the inorganic materials, several new compounds were synthesized, for example, in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system and in the heteropoly-nuclear acids and salts. The findings during the first phase of the contract warranted further work in each of the areas. This work was planned to be an extension of the most promising areas disclosed in the first report period. With organic materials it was planned to pressurize further polymer types, carry out polymerizations under pressure, and attempt the polymerization of normally inactive materials. In the semiorganic class a more detailed study of the reaction of dimethyldicyanosilane was planned, along with studies of additional similar materials and phthalocyanine polymers. In the area of inorganic polymers it was planned to emphasize the study of iron sulfides, polynuclear sulfides, and various phosphates.

Details of these studies and the results are to be found in the following sections.

II. SUMMARY

Organic Polymers

Superpressure compression studies were conducted on polymers, monomers, and organic compounds, including different generic materials and several types of the same generic material. Studies have included polyethylenes, polyamides, styrene, polystyrene, methylmethacrylate, polymethylmethacrylate, polyunsaturated materials, and nonconventional monomers under compressions up to 100,000 atmospheres. The

*Ultrahigh pressure is here meant to be equal to or greater than 30,000 atm (new 1960 scale).

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majority of compressions were conducted at ambient temperature, although several heated runs were made during the preliminary and final phases of this study.

The most influential parameters within the target range of compression appear to be the polymer, the holding period, and the temperature. Results to date do not show any generalized pattern of behavior for polymers. Rather, the data suggest that each material may well have its individual response to compression.

Since compression-induced changes generally were small, exceedingly sensitive methods for evaluation were desired. The use of density-gradient columns for evaluation of compression-induced effects proved very satisfactory for detecting physical changes. No correlation, however, could be established between density and structural changes. Ultimately it was necessary to go to molecular-weight determinations and distribution for characterization of changes on a structural level.

Evaluation of the effects of compression on the molecular level for organic polymers indicates that degradation occurs with polystyrene and polycaprolactam under conditions studied. Polymethylmethacrylate, on the other hand, appears to crosslink under similar conditions to show an increased viscosity molecular weight and a corresponding shift in the molecular-weight distribution. While nominal increases in molecular weight were shown with treatment of polymethylmethacrylate, compressions using monomer-polymer systems showed considerably higher molecular weights.

Results of compression studies on polybutadiene systems were very interesting. Compression-induced changes in hardness and gel content indicate that crosslinking (vulcanization) was effected by the pressure treatment. Graft reactions appeared to take place with polybutadiene and methylmethacrylate under pressure.

Exceedingly interesting was the discovery of a surprisingly high reactivity of quinone under superpressure treatment. Compression gave a conversion to a nonvolatile material thermally stable to above 500 C. Infrared, differential thermal analysis, and solubility studies confirmed significant changes in the material. This reaction appeared sensitive to a threshold pressure, temperature, and the presence of catalyst.

Semiorganic Polymers

Five types of semiorganic monomers or low polymers were subjected to a variety of combinations of ultrahigh pressure and temperature to discover the conditions under which reaction would occur. The research was undertaken to determine whether new polymerization reactions could be achieved or known polymers modified in such a way as to improve their properties.

It was hypothesized that dimethyldicyanosilane, $(\text{CH}_3)_2\text{Si}(\text{CN})_2$, might be polymerized by extreme pressure through conversion of the C = N groups to doubly or singly bonded carbon-nitrogen structures. This compound has proved to be extraordinary in that it reacts at lower temperatures as the pressure is increased. Polymerization has been achieved at room temperature when the pressure reaches 105,000 atmospheres. In a sealed tube under its own vapor pressure, a temperature of 200 C is required to

obtain the same effect. The product is an insoluble brown-to-black polymeric solid which decomposes slowly above 200 C at atmospheric pressure. Its composition is dependent on the pressure employed, with less rearrangement apparently occurring as pressure is increased. It appears that the presence of oxygen is necessary for the reaction to occur, and there are indications that the oxygen serves as a crosslinking agent between chains. Structures which fit the experimental data for these products have been proposed.

Four low polymers with Al-O-Si bonding (aluminosiloxanes) with either acetylacetone or isopropoxide bonded to the aluminum and with methyl, ethyl, or phenyl groups on the silicon were examined for reactivity over a range of pressures and temperatures. No significant effect of pressure was noted at temperatures below 200 C. At this temperature and above, ultrahigh pressure stabilizes the aluminum-oxygen-carbon bonding which exists at the acetylacetonate or isopropoxide linkages. The rupture of silicon-carbon bonds is also inhibited by the extreme pressure, and in some cases all reaction is prevented.

An arsenosiloxane formed from trivalent arsenic and having phenyl groups attached to the silicon was also studied. This material is reported to have the structure $\text{As}[\text{OSi}(\text{C}_6\text{H}_5)_2\text{O}]_3\text{As}$ and is thermally stable to 500 C at atmospheric pressure. In this case ultrahigh pressure had the effect of promoting decomposition via the breaking of silicon-carbon bonds at 500 C. An arsenosiloxane based on pentavalent arsenic, $(\text{HO})_2\text{AsO}[\text{OSi}(\text{C}_6\text{H}_5)_2\text{OAsO}(\text{OH})]_n\text{OH}$, was stabilized somewhat by increased pressure at 100 C. Nevertheless, it underwent pyrolysis rather than polymerization when pressurized at 200 C.

Pressurization of mixtures which are known to form phthalocyanine polymers of low molecular weight under ordinary conditions seemed to offer promise of increased molecular weight if moderate rather than ultra pressures are used and the system is catalyzed. Less reaction was observed as the pressure increased. Pressurization without the catalyst resulted in formation of urethane type structures.

Experiments with aluminum phenoxide, $\text{Al}(\text{OC}_6\text{H}_5)_3$, have indicated that pressure does not effect any reaction that cannot be obtained simply by heating.

Inorganic Polymers

The belt ultrahigh-pressure high-temperature apparatus was used in an exploratory program on the effect of ultrahigh pressure and simultaneous sustained temperature on inorganic materials. The apparatus was modified by using a 2 in. OD tungsten carbide die as opposed to the 2.5 in. OD die used previously. In addition, more massive binding rings were used with the modified apparatus. Both 12- and 4-degree dies were used interchangeably. The modified apparatus was calibrated by means of the electrical-resistance transitions in bismuth: Bi I-II at 25,000 atmospheres and the Bi V-VI at 87,000 atmospheres. The modified apparatus is linear to at least 100,000 atmospheres and it has about the same efficiency as the original apparatus. The modified apparatus can be used routinely at sustained high temperatures up to 1500 C to about 95,000 atmospheres. The equipment has been used at high temperature between 95,000 and

110,000 atmospheres but the frequency of failure increases exponentially above 95,000 atmospheres.

During the latter part of the program girdle dies and pistons were acquired for use on this project to extend the pressure-temperature range of the experimental work. Using a one-piece pyrophyllite gasket, the apparatus was found to be as efficient as the modified belt apparatus. Pressures of 120,000 atmospheres have been achieved in this device and preliminary results suggest that pressures of 140,000 atmospheres might be achieved by using plastic sheaths on the piston-gasket interface.

Exploratory high-pressure high-temperature experiments on iron monosulfide of stoichiometric (troilite) and nonstoichiometric (pyrrhotite) composition have shown that (1) there is a tendency for these materials to converge to an equilibrium composition under pressure, and (2) pressure will modify the position of the equilibrium boundary between iron monosulfide and iron disulfide. High-pressure high-temperature experiments on Sb_2S_3 , As_2S_3 , Bi_2S_3 , Ag_3SbS_3 , HgS , and PbCuSbS_3 gave negative results.

A new high-pressure hydroxyl-bearing form of aluminum phosphate was synthesized at high pressure and high temperature from anhydrous AlPO_4 (quartz structure) + H_2O and from hydrated AlPO_4 . The new phase is stable from 23,000 atmospheres at 600 C to at least 110,000 atmospheres at 1300 C. The density of the new phase is 3.10; it is 18 per cent denser than the quartz form of AlPO_4 . The p-t equilibrium boundary between the quartz form of AlPO_4 and the new phase in the presence of water was determined. Some data on the melting behavior of this system under pressure was also obtained. The new phase was characterized by complete chemical analysis, X-ray powder diffraction, optical crystallography, and infrared absorption spectroscopy. The coordination of both aluminum and phosphorus in the quartz form of AlPO_4 is 4, but the analytical results suggest that the new phase is an orthophosphate with phosphorus in fourfold coordination and aluminum in sixfold coordination. A tentative structural formula is $[\text{Al}_2(\text{PO}_4)_2 \cdot \text{Al}(\text{OH})_3]$. The new phase appears to be structurally related to the lazalite-scorzalite-barbosalite series: $[\text{Al}_2(\text{PO}_4)_2 \cdot \text{Mg}(\text{OH})_2] - [\text{Al}_2(\text{PO}_4)_2 \cdot \text{Fe}(\text{OH})_2] - [\text{Fe}_2(\text{PO}_4)_2 \cdot \text{Fe}(\text{OH})_2]$. A ferric iron structural analogue of the high-pressure aluminum phosphate has also been synthesized between 15,000 and 50,000 atmospheres from hydrated ferric phosphate. It probably has the formula $[\text{Fe}_2(\text{PO}_4)_2 \cdot \text{Fe}(\text{OH})_3]$. This phase is almost opaque but will transmit light when less than about 10 microns in thickness. It exhibits strong pleochroism, intense absorption, and extreme dispersion of the optic axes and bisectrices.

Between 50,000 and 110,000 atmospheres hydrated ferric phosphate transforms to a colorless unique new high-pressure phase which has been characterized by X-ray powder diffraction, optical crystallography, and infrared absorption spectroscopy.

Zirconium pyrophosphate (ZrP_2O_7) is a cubic material which transforms to a new high-pressure phase above about 45,000 atmospheres and is stable to at least 105,000 atmospheres at 1000 C. The new phase is about 15 per cent denser than the cubic form and has been characterized by X-ray powder diffraction, optical crystallography, and infrared absorption spectroscopy. Molar refraction data and the infrared data indicate that the cubic and the high-pressure polymorphs are derived by differences in the stacking of the coordination polyhedra rather than by differences in primary coordination.

III. EXPERIMENTAL SECTION - ORGANIC POLYMERS

Introduction

Studies were conducted during this program on the effects of superpressure treatment, primarily at ambient temperature, on the structures of four general types of organic systems. These included polymers, monomer-polymer systems, monomers, and multifunctional chemical compounds not generally considered to be monomers.

The supporting technique for evaluating pressure-induced structural changes generally was molecular-weight measurement and molecular distribution in the case of polymeric materials. However, thermal data, hardness, infrared, and differential thermal analysis were also used for studying changes in several materials.

Although most references to reactivity under pressure relate to the use of elevated temperature and frequently the use of catalysts, Gonikberg and Zhulin^{(1)*} report the polymerization of butyraldehyde and isobutyraldehyde at high pressures. Yields of these polymeric materials in the order of 60 to 70 per cent were obtained under compressions of 6200 kg/sq cm; lower pressures, however, were less effective. Benzoyl peroxide catalyst was effective in increasing rate, but such catalysis resulted in lower molecular-weight material.

Work was reported by Shchetinin, et al.,⁽²⁾ in which polymerization of arylcyclopropanes was studied under high pressures and temperature. Polymerization was obtained with p-hydroxy- and p-methoxyphenylcyclopropane under 200 C and 500 to 7500 atmospheres. No polymerization was obtained with phenylcyclopropane or with its derivatives with chlorine, amine, and dimethyl amino substituents in the para position.

Other polymerization studies under elevated pressures have been reported for cyclic unsaturated hydrocarbons, propargyl alcohol, and ethylene. The polymerization of bicyclo-[2,2,1] heptane-2, bicyclo [2,2,1] heptadiene-2,5, and cycloheptatriene was studied by A. M. Polyakova.⁽³⁾ Polymerization of these materials was investigated under 6000 atmospheres using t-butylperoxide as catalyst. Temperature of the pressure polymerization ranged from 130 to 200 C. Polymer with the highest softening point was prepared at 200 C. For these materials, pressure polymerizations appeared to give increased molecular weight and yield as temperature is increased.

The polymerization of propargyl alcohol under pressures of 1000 to 6000 atmospheres was investigated by Polyakova⁽⁴⁾. It was reported that this alcohol undergoes thermal polymerization under pressure with the formation of polymers containing conjugated bonds. Polymerization of ethylene under pressures to 20,000 atmospheres at temperatures to 200 C in the presence of a catalyst and a solvent was disclosed.⁽⁵⁾ Improved physical properties are claimed for this material which melts at 127 to 132 C and is more crystalline than conventional polyethylene.

A review on "Addition Polymerization at High Pressures" by Weale⁽⁶⁾ discusses the results of other polymerization studies covering a wide range of monomers. The range of pressures investigated generally was limited to 10,000 atmospheres. Even in this range, differences were observed in the polymerization behavior of monomers

*References are listed on page 84.

under pressure. Thus, the polymerization rate of styrene was shown to increase with pressure in the range studied (to 5,000 atmospheres). Concurrently, molecular weight was shown to increase to about 3000 atmospheres and to remain relatively constant above this. Polymerization of α -methyl styrene was shown to have a sharp maximum in the rate of polymerization as a function of pressure. This was attributed to solidification of the monomer under pressure, and above this, only a dimer was produced.

Since the samples employed in the superpressure study were limited in size, techniques were selected which were reasonably well established and required only small quantities of material. Molecular-weight determination through viscosity changes in a solvent-polymer system appeared to be the best suited for this study. The equipment of Shulkin and Sparks⁽⁷⁾ was used successfully with minor modifications in techniques.

The most useful procedure for the determination of molecular-weight distribution appeared to be the turbidimetric titration method developed by D. R. Morey.^(8,9) Modifications of this method were devised for polystyrene and polymethylmethacrylate. Some difficulty was encountered in developing a suitable system for use with polycaprolactam, but techniques were devised to overcome the problems.

Experimental Results

Compression Studies

The major amount of effort in the organic polymer compression program was conducted at ambient temperature using pressurizing techniques reported previously (ASD-TDR-62-73). However, several heated runs were made toward the end of the program to try to accelerate reactivity in catalyzed systems and in the nonmonomer experiments. The belt apparatus was used for most of the work. However, the girder apparatus was used later in the program to permit more efficient press use and to obtain higher compression.

Effect on Polymers. Polymer-compression studies constituted a minor effort during this period. Some runs were made, however, to complete unfinished studies and to provide correlation data. Much of the work with compressed polymers was to develop analytical techniques and to verify compression-induced structural changes. Thus, many of the polymers discussed were compressed early in the program and re-evaluated during this period.

Initially, compression effects were monitored by means of density change determined in density gradient tubes. It is interesting to note that consistent patterns of behavior were observed for different materials, but similar behavior was shown for generically similar materials. Thus, density-compression data obtained for several different types of polymers under comparable conditions are summarized in Figure 1. Results are too limited to present as a rigorous picture of polymer behavior under compression. It is believed, however, that some correlation is shown and some generalizations may be postulated. Within the range of about 40,000 to 70,000 atmospheres, high- and low-density polyethylene show parallel behavior as might be expected.

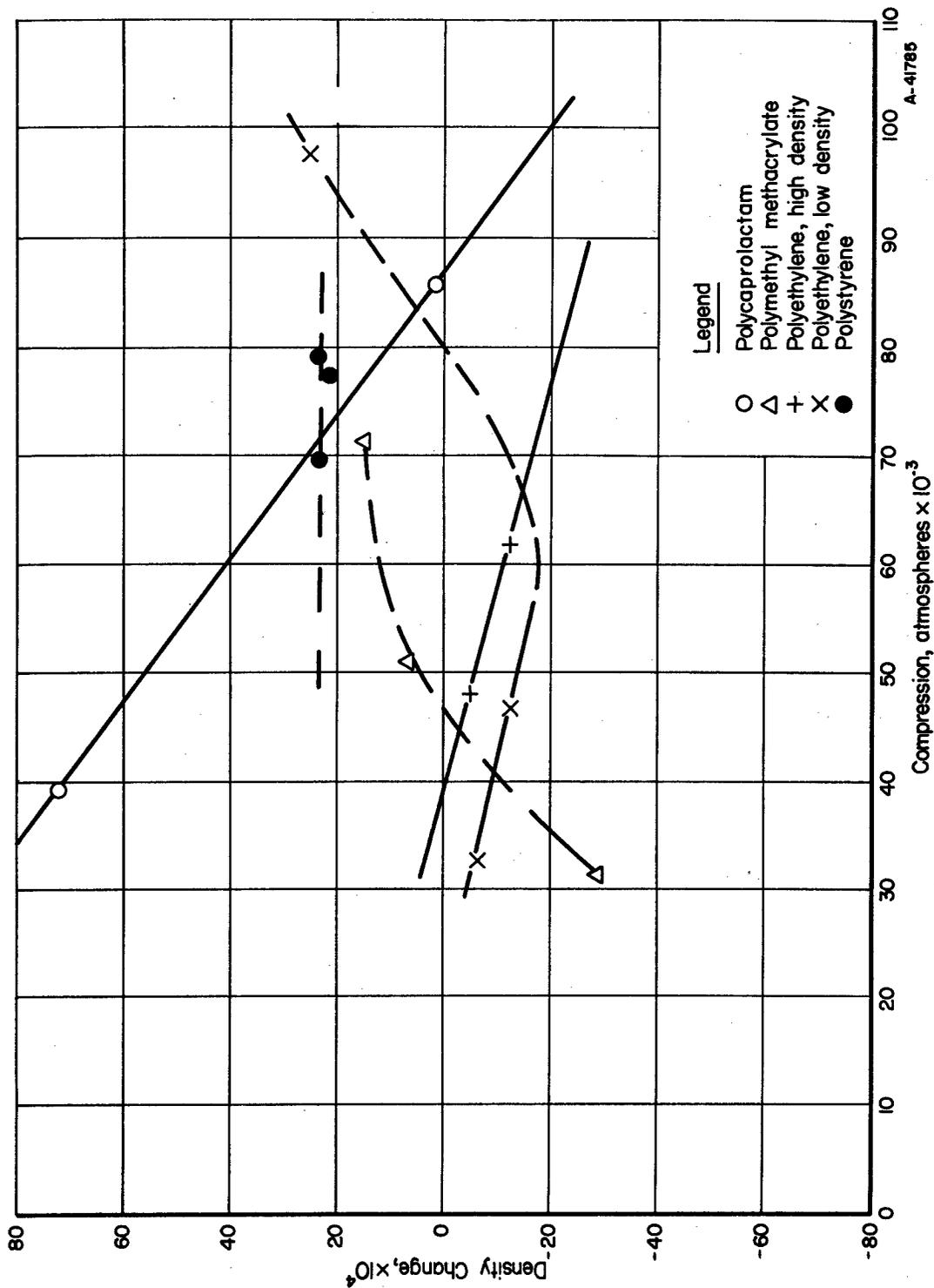


FIGURE 1. EFFECT OF POLYMER TYPE ON SUPERPRESSURE BEHAVIOR

Compression holding period — 60 minutes.

Low-density polyethylene deviated from this pattern at 100,000 atmospheres and showed a significant density increase. Comparable data are not available on high-density material to determine whether the initial parallel behavior is continued.

The greatest density-compression effects were shown for polycaprolactam and polymethylmethacrylate. Polycaprolactam showed a density increase under low compressions around 40,000 atmospheres, but increasing compression appeared to be less effective in raising polymer density. Around 85,000 atmospheres, the density appeared to be nearly unchanged from the original.

Polymethylmethacrylate, on the other hand, showed a tendency to increase in density with increasing compression in the range of 30,000 to 70,000 atmospheres.

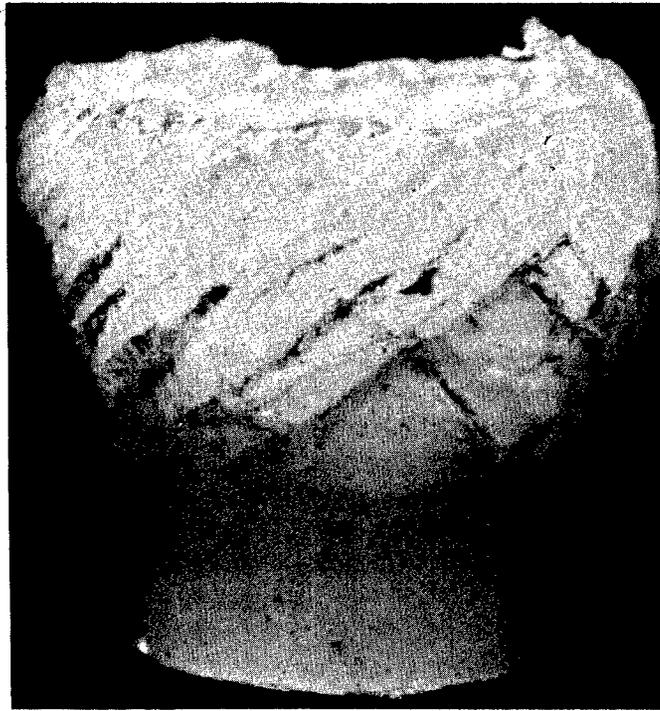
Polystyrene compressions showed some increase in density; however, the observed increase appeared relatively constant over a broad range of times and compressions.

Data available for use in this correlation are limited. Consequently, Figure 1 must be considered qualitative at best, but it is interesting to note that there do appear to be generic differences in behavior. Although considerable care is exercised to maintain comparable operation and to exclude factors which might void the correlation, it must be emphasized that the changes measured are extremely small.

Inspection of the correlation shown in Figure 1 suggests the following possibilities:

- (1) The resonance structure of polystyrene may exert a stabilizing influence under the conditions of current study.
- (2) The polymethylmethacrylate may be exhibiting evidence of activation as shown by the increasing density as the compression is increased in the current range.
- (3) Low-density polyethylene also may be showing evidence of some reactivity at the higher compression range.
- (4) Polycaprolactam appears to increase in density with prolonged treatment at moderate compressions and to decrease in density under higher compressions.

Normally, polycaprolactam is recovered from a compression run as a discrete although slightly deformed cylinder. However, during the course of normal decompression of Run 18837-4a, a blowout occurred which instantaneously dropped the loading from 60 tons to 30 tons. Examination of the system after completion of the otherwise normal decompression procedure indicated that probably all loading on the sample was lost during the blowout, except for the assembly remaining on the opposite side of the die. A photomicrograph of the sample, Figure 2 shows extreme swelling of the specimen at the blowout. The restrained end of the sample appears relatively normal, but the expanded end shows very marked slip planes induced in the sample by the treatment. Similar slip-plane markings were evident in a sample of compressed polymethylmethacrylate (Figure 3). The latter material appears to be very sensitive to loading and



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FIGURE 2. APPEARANCE OF POLYCAPROLACTAM SAMPLE AFTER BLOWOUT



FIGURE 3. COMPRESSED POLYMETHYL METHACRYLATE SHOWING SLIP PLANES

unloading rates. Compression is very frequently accompanied by loud snapping noises which occasionally were mistaken for die damage. Very slow decompression appears necessary to minimize sample cracking.

Following photomacrographic study of the polycaprolactam sample, a series of density studies was conducted on the sample. Results of this work are shown in Table 1. The gross sample shows considerably greater reduction in density than subsequent sections. It is likely that disruptive decompression resulted in voids within the sample and between slip planes. Although all samples are prewet by evacuation under a gravity-adjusted liquid to minimize the effect of surface voids, it may well be that the first pre-wetting did not completely reach all voids. Subsequent sectioning permitted access to the deeper recesses with a subsequent increase in the relative sample density. Thus, while the gross samples showed a negative density change of 0.0032 gram, the half-section only showed a negative density change of 0.0018 gram. The half-sample was subsequently sectioned to determine the density profile from the exploded to the restrained end. It is believed significant that a density profile was shown in which the section adjacent to blowout was lowest and the restrained end highest. This would seem to confirm suspicions of the importance of decompression rate. This instance is an extreme situation, but it validates the necessity of using a constant decompression procedure in running comparative studies of the effects of compression on polymer properties.

TABLE 1. EFFECT OF BLOWOUT ON POLYCAPROLACTAM DENSITY

Maximum load, tons			140
Compression, atm x 10 ⁻³			91
Compression period, min			2
Load before blowout (est), tons			60
Load after blowout, tons			30
	Density		
	<u>Initial</u>	<u>Final</u>	<u>Density Change</u>
Gross Sample	1.1456	1.1424	-0.0032
Half-Section	1.1456	1.1438	-0.0018
Blowout Section	1.1456	1.1447	-0.0009
Intermediate Section	1.1456	1.1451	-0.0005
Restrained Section	1.1456	1.1489	+0.0033

Viscosity molecular weights and molecular-weight distributions were determined for controls and selected samples of compressed polystyrene, polymethylmethacrylate, and polycaprolactam. Results of these determinations (Table 2) show changes both in molecular weight and molecular-weight distribution which are attributed to the compression treatment.

However, these attempts to correlate the observed density changes, molecular weights, molecular-weight distributions, and compression data were unsuccessful. Although density-change patterns could be related to compression for different materials as previously shown, results indicate that these changes do not reflect the changes in molecular composition. Thus, it appears that density data reflect either physical changes in the polymer or an unresolved compression parameter.

TABLE 2. CORRELATION OF POLYMER STUDIES WITH COMPRESSION TREATMENT

Polymer Run	Maximum Compression,		Holding Time, min	Density Change	Viscosity Molecular Weight
	atm x 10 ⁻³	Control			
Polystyrene 18205-93	Control	None	None	None	230,500
	70	+0.0025	30		208,000
18837-32	74	Monomer-polymer	1450		129,000
Polymethylmethacrylate 18205-94	Control	None	None	None	72,800
	31.5	-0.0014	60		153,000
18205-96	71.5	+0.0015	60		140,000
Polycaprolactam	Control	None	None	None	21,800
	35	-0.0025	1		21,600
18205-31-10B	10	+0.0026	2		21,600
18837-4(I)	39	+0.0072	60		20,400

Primarily high-molecular-weight material
 High molecular weight equivalent to control; evidence for low molecular weight
 Less high-molecular-weight material than control; evidence of low molecular weight
 Evidence for broad range of polymers
 High- and intermediate-molecular-weight polymers
 High- and intermediate-molecular-weight polymers
 Evidence for several fractions of polymers over broad range
 Evidence for polymer fractions comparable to control, but less high-molecular-weight and more low-molecular-weight material
 Evidence for similar number of fractions; low-molecular-weight material less prominent than previous run, but intermediate material more prevalent
 Reduction in high-molecular-weight fraction and accentuation of intermediate- and low-molecular-weight fractions

Results indicate that viscosity molecular-weight determination and molecular-weight-distribution studies are more valuable methods of appraising the effect of compression on polymeric materials. It is interesting to note that evidence was obtained for reactivity under compression for polymethylmethacrylate polymer.

It was projected that a polymer such as polybutadiene might be more active because of the residual unsaturation possibly providing reaction sites. Several compression experiments were conducted with polybutadiene and polybutadiene-monomer systems to verify this postulation. Results of these studies, Table 3, are encouraging in that invariably the character of the starting material is markedly changed. The un-squeezed polybutadiene is a soft, tacky, easily cut material. After compression alone and in the presence of methylmethacrylate and styrene monomers, the material is harder, tack-free, and considerably more cut resistant. The extent of the monomer-polymer interreaction is uncertain, since these runs were made in the girdle apparatus and evidence of monomer leaks was observed at the conclusion of the runs.

TABLE 3. EFFECT OF SUPERPRESSURE TREATMENT AT AMBIENT TEMPERATURE ON POLYBUTADIENE SYSTEMS

Run	System	Estimated Maximum Compression, atm x 10 ⁻³	Holding Time, hr	Benzene Solubility ^(a)	Durometer Hardness	Remarks
Control	Polymer	--	--	Soluble	32	Tacky, easily cut
19433-7	Polymer	50	24	Insoluble	47	Nontacky, tough
19433-36	Polymer	100	25	Insoluble	60	Nontacky, tough
19433-14	Methylmethacrylate/polymer (0.33 volume)	80	16	Insoluble	55	Nontacky, tough, capsule leak
19433-16	Styrene/polymer(0.66 volume)	80	14-2/3	Insoluble	40	Nontacky, tough, capsule leak

(a) Benzene dissolution was started preparatory to running intrinsic viscosities. Little crosslinking was present in the control, as shown by rapid and virtually complete solubility. After 60 hours' extraction, compressed samples were swollen by benzene but were still intact.

Since the Staudinger constants for polybutadiene and these reaction products are not known, an attempt was made to evaluate the respective molecular-weight changes through intrinsic-viscosity measurements. The crosslinked content of the control was very low as evidenced by the rapid and virtually complete dissolution in benzene. Attempts, however, to obtain equivalent dissolution with compressed samples were unsuccessful. Polymer characterization was confined to physical-property measurements, determination of gel content, and intrinsic-viscosity determination of the extracted portion as shown in Table 4.

Thus superpressure treatment of polybutadiene shows evidence of compression-induced reactivity. Prior to compression, the material had a durometer hardness of 32, was tacky to the touch, and was easily cut with a razor blade. However, after a 16-hour compression, the sample had a durometer hardness of 47, was no longer tacky, and was very cut resistant.

TABLE 4. CHARACTERIZATION OF SUPERPRESSURE-TREATED POLYBUTADIENE SYSTEMS

Run	System	Estimated Maximum Compression, atm x 10 ⁻³	Holding Time, hr	Gel Content, per cent	Intrinsic- Viscosity ^(a) of Soluble Portion
Control	Polymer	--	--	26.5	1.52
19433-7	Polymer	50	24	85	1.23
19433-36	Polymer	100	25	64.2	1.7
19433-14	Methylmethacrylate/polymer (0.33 volume)	80	16	87	2.19
19433-16	Styrene/polymer (0.66 volume)	80	14-2/3	60	0.61

(a) Determined in benzene.

Also, results of compressions using polybutadiene and monomers suggest inter-reactivity in the system. The presence of methylmethacrylate apparently contributing to crosslinking in the nongel portion of the samples as shown by the increase in intrinsic viscosity. Styrene had a less beneficial effect, as shown by the lowered hardness and intrinsic viscosity. It would appear that graft reactions can be effected between reactive polymers and dissimilar monomers.

Effect on Monomer-Polymer Systems. Initial experiments involving encapsulated systems were on monomer-polymer systems to reduce the system fluidity, compressibility, and possible reactivity.

Work was initiated on this phase of the compression study using the system styrene-polystyrene. Polystyrene sample slugs (0.227 inch in diameter x 0.337 inch high) machined to fit into a lead foil can were predrilled and prechecked for densities.

The machined and drilled polystyrene sample was placed in the lead-foil can described in the Annual Report, ASD-TDR 62-73. The can was dropped into a snug-fitting aluminum chill block to minimize sample heating during soldering. The styrene-monomer was charged from a hypodermic syringe to the cavity in the center of the polymer. A pretinned lead-foil cap was placed on the lead can and soldered to the flange on the can with a pencil soldering iron. The completed encapsulation was pushed from the bottom to force it out of the chill block. The assembly height was adjusted to 0.345 inch and fitted into the superpressure assembly.

Three ratios (volume) of monomer to polymer were used: 0.12, 0.34, and 1.09. Previous to starting the monomer-polymer compression studies, encapsulated compression runs were made using polystyrene slugs alone. Results of this work provided the basis for the lead-can design and gave encapsulated-polymer calibration data. Immediately prior to making the liquid-polymer runs, calibration data were obtained on encapsulated polystyrene with a bismuth wire positioned between the silver chloride and pyrophyllite sleeves. Since the bismuth monitor could not be installed concentric to the sample in the runs containing liquid, it was planned to use the intersleeve placement of the monitor and extrapolate the results to estimate the sample compression.

It was postulated that trace catalytic materials in the polymer might be effective in initiating polymerization. It was believed, however, that, to be effective, prolonged compression likely would be required because of the exceedingly small concentration of possible catalysts.

Qualitative results of runs to date suggest that a change is occurring in the compressed system. Results, Table 5, show that, while control runs (i. e., encapsulation systems held overnight without pressuring) become sticky and tacky due to solution of the monomer in the polymer, compressed runs were rubbery and nearly free from a tacky character. Free styrene undoubtedly was still present in the compression runs, as evidenced by a strong styrene odor.

Density determinations were not made immediately on the compressed material. It was observed at the time of the density determinations that the samples had hardened considerably, presumably due to the loss of unreacted styrene. Greater density increases were noted in the monomer-polymer runs than were observed at any time previously with the compressed polymer. Among the possible explanations of this effect are: (1) the monomer polymerizes to a more dense form under the high pressure, (2) the monomer grafts to the preformed polymer to give a more dense structure, and (3) the solvent action of the monomer permits densification of the polymer under pressure to a greater extent than in the absence of the solvent. The absence of the polymer-solvent characteristics and the increased densities with higher monomer-to-polymer ratios in the compressed runs would seem to indicate some reactivity of the monomer.

Examination, however, of molecular-weight characterizations, Table 6, of styrene-monomer-polymer and polymer systems shows that these density increases are not reflected in increased molecular weights; hence the density factors must be physical packing.

A comparison of the effect of compression on methylmethacrylate monomer-polymer and polymer systems is shown in Table 7. In general, viscosity molecular weights increase slightly with compression treatment, irrespective of the density behavior for polymethylmethacrylate. This tendency to increase in molecular weight suggests a crosslinking mechanism which appears to be confirmed by the significant increase in molecular weight during compression in the presence of monomer.

Effect on Monomer Systems. The high degree of monomer reactivity, especially with methylmethacrylate, in the monomer-polymer studies suggested that a high order of reactivity might be expected in the monomer polymerization program. Initial experiments, with encapsulated, catalyzed, purified, monomer systems used small quantities of catalyst to minimize the possibility of a runaway reaction. Considerable difficulty was encountered with ruptured capsules and consequent leakage. Initial experiments were conducted with azodiisobutyronitrile. Azodiisobutyronitrile (AIBN) is a good catalyst for methacrylate polymerization, but, under normal activation conditions, requires heating to effect decomposition and catalytic reactivity. It is of interest in this connection to cite the work of Gonikberg and Zhulin⁽¹⁾ on the polymerization of aldehydes at high pressures. Their work at room temperature and high pressures showed that AIBN had no effect on the normal reactivity of these compounds. Benzoyl peroxide, however, was effective in increasing the reaction rate at room temperature and elevated pressures. It also is interesting to note that these researchers found that an induction

TABLE 5. ENCAPSULATION STUDIES USING STYRENE POLYSTYRENE SYSTEM

Run	Press Load at Bi-I-II Transition, tons	Maximum Compression, atm x 10 ⁻³	Compression Period, min	Vol Monomer Vol Polymer	Density		Remarks
					Initial	Final	
18205-82	46.25	79	60	No monomer	1.0516 ^(a)	1.0532	(b)
18205-84	45.5	77	60	No monomer	1.0480 ^(a)	1.0502	(b)
18205-83	41.25	79	30	No monomer	1.0507 ^(a)	1.0502	(c)
18205-93	--	70	30	No monomer	1.0486	1.0511	
18837-26	44.5	65.5	1260	0.12	1.0511	1.0556	(d)
18837-26	Control	None	None	0.12	1.0480		(e)
18837-27	47.5	62.5	1260	0.34	1.0482	1.0522	(d)
18837-27	Control	None	None	0.34	1.0492		(e)
18837-32	42.5	72.5	1050	1.09	1.0484	1.0631	(d)
18837-32	Control	None	None	1.09	1.0446		(e)

(a) Qualitative values. Determination in solvent column was shown to result in error due to absorption of solvent.

(b) Control run. Monitor in center of sample.

(c) Control run. Monitor between sleeves.

(d) Rubbery solid when first opened. Tends to harden as styrene volatilizes.

(e) Control samples were softened by the solvent action of the styrene. The resulting systems were sticky and tacky after 1260 minutes. Although the lead can could be stripped from 18837-26 control, the cans could not be removed from the other two controls.

TABLE 6. RELATION OF VISCOSITY MOLECULAR WEIGHT AND INTRINSIC VISCOSITY FOR POLYSTYRENE

Run	$\frac{\text{Vol Monomer}}{\text{Vol Polymer}}$	Maximum Compression, atm x 10 ⁻³	Compression Period, min	Density, Final	Intrinsic Viscosity	Viscosity Molecular Weight
Control	No monomer	--	--	1.0486	0.960	230,500
18205-93	No monomer	70	30	1.0511	0.890	208,000
18837-32	1.09	72.5	1050	1.0631	0.625	129,000

TABLE 7. EFFECT OF SUPERPRESSURE TREATMENT AT AMBIENT TEMPERATURE ON METHYLMETHACRYLATE SYSTEMS

Run	System	Estimated Maximum Compression, atm x 10 ⁻³	Holding Time, hr	Density, Final	Intrinsic Viscosity	Molecular Weight	Remarks
Control	Polymer	--	--		0.404	111,000	Plexiglass VM
	Extruded rod	--	--	1.1900	0.442	125,000	Ditto
18205-94	Polymer	31	1	1.1886	0.512	153,000	--
18205-96	Polymer	71.5	1	1.1916	0.480	140,000	--
19433-10	Polymer	98	2	--	0.473	137,000	--
19433-5	Monomer/polymer (0.34 volume)	45	34	--	0.804	284,000	--

period and the presence of lead were effective in increasing the reaction rate. Accordingly, other polymerizations were conducted using benzoyl peroxide as a catalyst. Initial runs made in lead cans gave little indication of monomer reactivity. Experiments, therefore, were conducted to determine whether encapsulation components might be poisoning reactivity. Results indicated that the flux and lead both could be deleterious to styrene reactivity. However, satisfactory polymerization reactivity was obtained in control runs in the presence of stainless steel cans washed free of flux. Compression studies subsequently were conducted in stainless steel capsules sealed with a minimum of solder and washed several times to remove all traces of flux. Evidence of some polymerization was finally obtained in these carefully washed stainless steel cans. However, significantly more catalyst and prolonged heating were required to produce partial polymerization of styrene in contrast to the conditions required to produce solid polymer in control runs. Results of control and compression studies for methylmethacrylate and styrene are summarized in Tables 8 and 9.

It would seem from these results that lead is an inhibitor for benzoyl peroxide catalyzed styrene polymerizations. This is not unreasonable in that lead is recognized as a free-radical trap. The apparent inhibiting effect of superpressure on the polymerizations studied was not anticipated. Several postulations can be suggested to account for the apparent anomaly between the reactivity of monomer in polymer and catalyzed monomer systems.

- (1) Residual free radicals and compression-induced free radicals in polymers such as polymethylmethacrylate appear to react readily with available monomer in a chain propagation mechanism to give increased molecular weights; the styrene-polystyrene system appears to react by chain degradation and termination mechanisms to give lowered molecular-weight material under the conditions studied.
- (2) Superpressure treatment of polymeric materials causes mechanical fracture of the polymer chain to produce a reactive site, but similar compression of a catalyzed liquid system may repress the fragmentation of conventional catalysts, thus requiring a higher activation energy in order to become functional.
- (3) The compression used in these studies may produce sufficient increase in monomer viscosity or possibly solidification such that the orientation and immobility of the monomer militated against polymerization propagation.

These latter postulations are supported by the recent publication by Weale⁽⁶⁾ in which the pressure dependence of catalyst decomposition was reviewed. It was shown that the unimolecular decomposition of benzoyl peroxide in carbon tetrachloride is retarded by pressure. The equilibrium constant at 3000 atmospheres was reported to be about half the value at 1 atmosphere. Thus, projection of this behavior to the extreme loading in the present study would tend to reinforce the validity of the postulation.

The freezing behavior of α -methyl styrene with pressure also was reviewed. The freezing point of this monomer was shown to increase linearly from -23.2 C at 1 atmosphere to 60 C at 4860 atmospheres. It seems very likely that at 100 C styrene may be frozen under the compressions used.

TABLE 8. EFFECT OF SUPERPRESSURE TREATMENT ON CATALYZED METHYLMETHACRYLATE SYSTEMS

Run	Catalyst		Press Load, tons	Holding Time, hr	Estimated Temperature, C	Remarks
	Material	Per Cent				
19433-6	None		120	17	Ambient	Lead capsule leaked, no evidence of polymer
19433-11	Azodiisobutyronitrile	0.05	160	16	Ambient	Lead capsule leaked, no evidence of polymer
19433-22	Benzoyl peroxide	0.15	58	4-1/2	Ambient	No evidence of polymer in liquid in lead capsule
19433-23	Benzoyl peroxide	0.15	80	18	Ambient	No evidence of polymer in liquid in lead capsule
19433-29	Benzoyl peroxide	0.20	78	2	100	No evidence of polymer in liquid in stainless capsule
19433-31	Benzoyl peroxide	0.20	80	16	100	Decompression blowout, tacky material remaining in stainless capsule

TABLE 9. EFFECT OF SUPERPRESSURE TREATMENT ON BENZOYL PEROXIDE CATALYZED STYRENE SYSTEMS

Run	Catalyst, per cent	Press Load, tons	Holding Time hr	Estimated Temperature, C	Remarks
Control	0.2	--	2	80	Solid polymer, reaction in glass vial
Control	0.2	--	2	80	Solid polymer, reaction in stainless can
Control	0.2	--	2	80	Viscous liquid, reaction in lead can
Control	0.2	--	2	80	Viscous liquid, flux in vial
19433-32	0.2	78	14-1/2	100	No evidence of polymer in stainless capsule
19433-37	0.2	80	21	100	Small amount of viscous liquid in stainless capsule
19433-41	0.7	100	14-1/2	100	No evidence of leak during run, viscous, tacky, product in stainless capsule
19433-42	3.0	110	89	Ambient	No evidence of leak, no evidence of polymer
19433-42 Control	3.0	--	89	Ambient	No evidence of polymer in glass vial

Consistent with these postulations it would be interesting to verify the effect of superpressures on catalyst decomposition rates. It also would be of interest to study the effect of monomer compression in the presence of different permanent radical-containing compounds to see whether these used with pressure could produce significant monomer activation. It also would be of interest to determine optimum pressure-temperature conditions needed for different monomer-catalyst systems.

Effect on Nonmonomers. Possibly the area of greatest interest and promise is that of pressure-induced reactivity of nonmonomers. Experimental superpressure work was initiated with several compounds which possess potentially reactive groups, but which normally do not give (high-molecular-weight) polymers. Since polymerizations have been reported^(1-4,6) for several aliphatic multifunctional compounds under elevated pressures and temperatures, aromatic compounds with similar functionality were selected to take advantage of possible ring-induced stabilization. Compounds studied in this series have included aromatic compounds containing carbonyl, hydroxyl, carboxyl, and (-CHO) and combinations of nonmonomers with conventional monomer systems.

No change was noted in the thermal behavior or appearance of any of the compounds studied except quinone (Table 10). The compressed material was observed to be darker and to have a slightly higher melting or softening point and then subsequently appeared to become solid. It is likely that the melting point observed was due to unreacted quinone. Infrared and differential-thermal-analysis studies conducted on several products verified the reactivity and provided some structural data. Samples of the products purified by heating above the sublimation temperature of quinone for 3 hours reverted to a light-yellow color. Data on the treatment indicated that varying conversions of the quinone to nonvolatile compounds had been obtained which appear to correlate with the compression conditions. Comparison of the infrared spectra of quinone (Figure 4) and a heat-purified product (Figure 5) confirms a chemical change. Data are not sufficient to project the reaction mechanism with certainty. However, the presence of new absorption bands in the product at 6.8, 8.4, and 12.3 microns suggests that aromatic ether and phenolic hydroxyl groups were formed during the reaction. Similar absorptions were shown for several runs.

The use of heat and compression, however, does produce a product with a spectral pattern (Figure 6) which is different from that of both the quinone and compressed quinone. In addition to the absorptions shown by the compressed quinone, strong absorptions were recorded at 9.4 and 10.6 microns.

It is very interesting to note that the spectra (Figure 7) from a sublimation-purified sample of compressed and heated quinone-methylmethacrylate-benzoyl system was very similar to the spectra of the compressed, unheated quinone. It also seems highly significant that the unreacted quinone in this system was quite low. It is not known definitely whether the methylmethacrylate catalyst system entered this reaction or whether the reactivity was due primarily to the quinone-benzoyl peroxide system. Since there is virtually no spectral evidence for the presence of polymethylmethacrylate in this product, it is suspected that the monomer may have volatilized and not contributed significantly to the product. This is further strengthened by the results in Run 19433-25 in which monomer was added to the reaction. This compression gave very little non-sublimable product. However, neither did a similar compression of quinone alone.

TABLE 10. EFFECT OF SUPERPRESSURE TREATMENT ON NONMONOMER SYSTEMS

Run	System	Press Load, tons	Holding Time, hr	Estimated Temperature, C	Thermal Behavior		Remarks
					Before Compression	After Compression	
194338-8(a)	Anthraquinone	120	24-1/2		Sublimes 285 C	Sublimes 285 C	--
19433-12(b)	Catechol	140	16		Melts 105 C	Melts 105 C	--
19433-13(b)	Phthalaldehydic acid	140	6		Melts 97-97.5 C	Melts 97-98 C	--
19433-9	Quinone	110	18-1/2		Melts 115 C	Melts and solidifies 120-122 C	Differences noted in infrared(e)
						Reaction at 500 C	Differential thermal analysis(f)
19433-24(a)	Quinone	82	44-1/2	R. T.	Melts 115 C	Melts and portion solidifies	14% nonsublimable
19433-28(a)	Quinone	82	2	100	Melts 115 C	Color changes with different temperatures	3. 3% nonsublimable
19433-33(a)	Quinone	190	21	R. T.	Melts 115 C	Color changes with different temperatures	14. 1% nonsublimable
19433-25(a)	Quinone Methylmethacrylate	82	16-1/2	R. T.	--	--	15. 7% nonsublimable
19433-26(a)	Quinone Methylmethacrylate Benzoyl peroxide (0. 15 per cent)	65	2	100	--	Volatilization at 230-240 C	2. 9% nonsublimable
19433-30(c)	Benzoic acid	80	18	100	Melts 122 C	Black residue	94. 6 per cent sublimation at 100 C
19433-34(d)	Phenolphthalein	80	15-1/2	100	Melts 261 C	Melts 261-265 C	No change

(a) Lead capsule squeezed in belt apparatus.

(b) Lead capsule squeezed in girdle apparatus.

(c) Stainless steel capsule squeezed in girdle apparatus.

(d) Stainless steel capsule squeezed in belt apparatus.

(e) New absorption bands at 6, 8, 4, and 12. 3 microns.

(f) Less endotherm at 100 C for the compressed product and introduction of an exothermic reaction around 500 C.

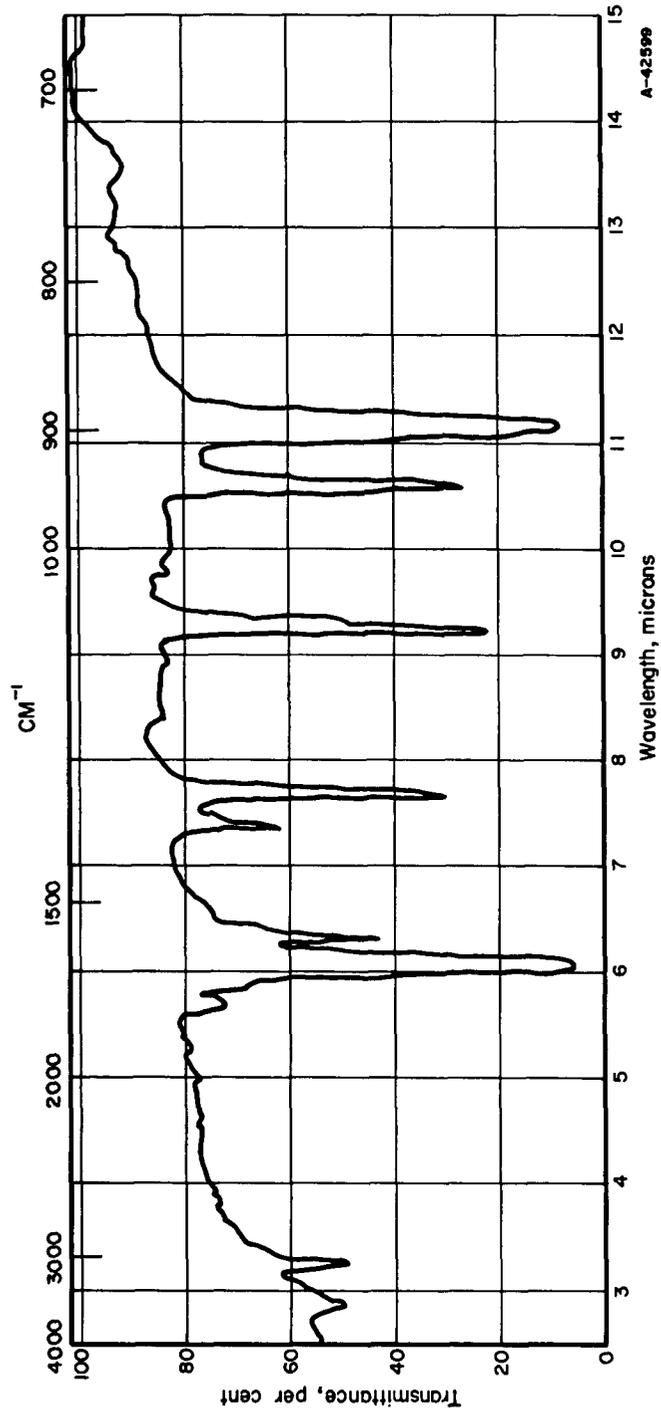


FIGURE 4. INFRARED SPECTRA OF QUINONE

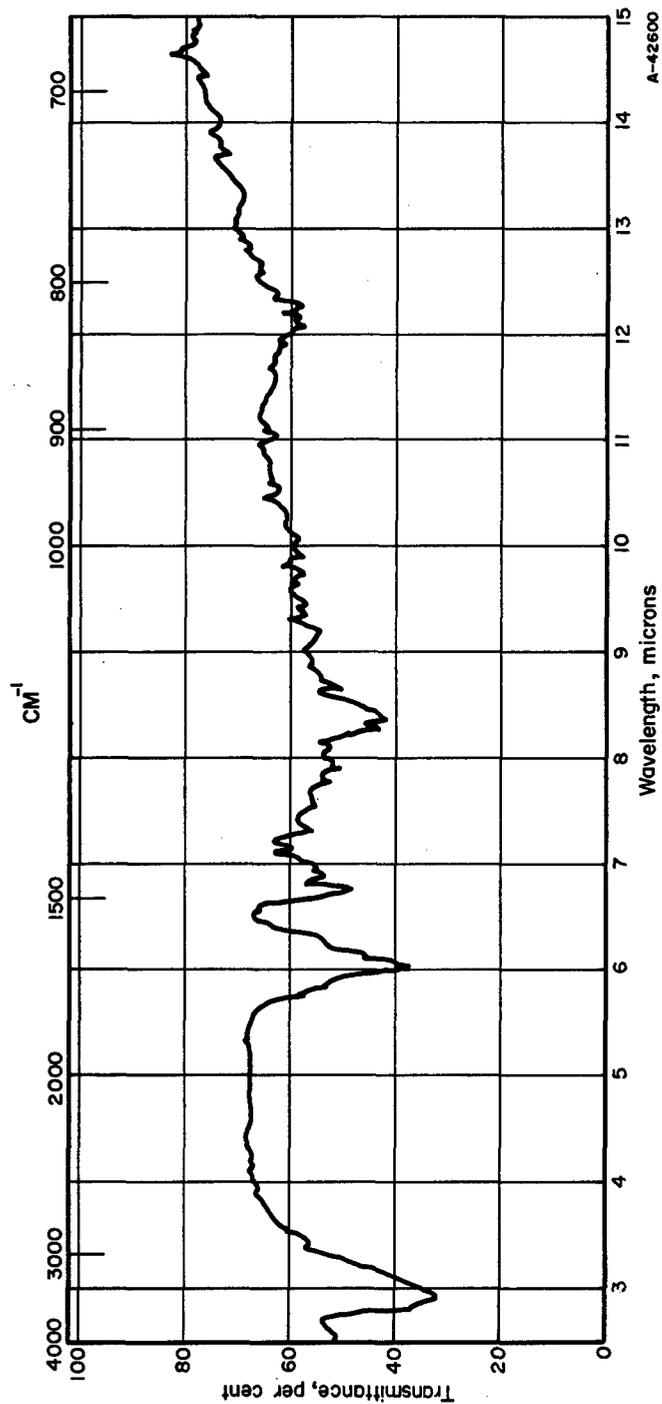


FIGURE 5. INFRARED SPECTRA OF HIGH-PRESSURE PRODUCT OF QUINONE AFTER
SUBLIMATION REMOVAL OF UNREACTED QUINONE

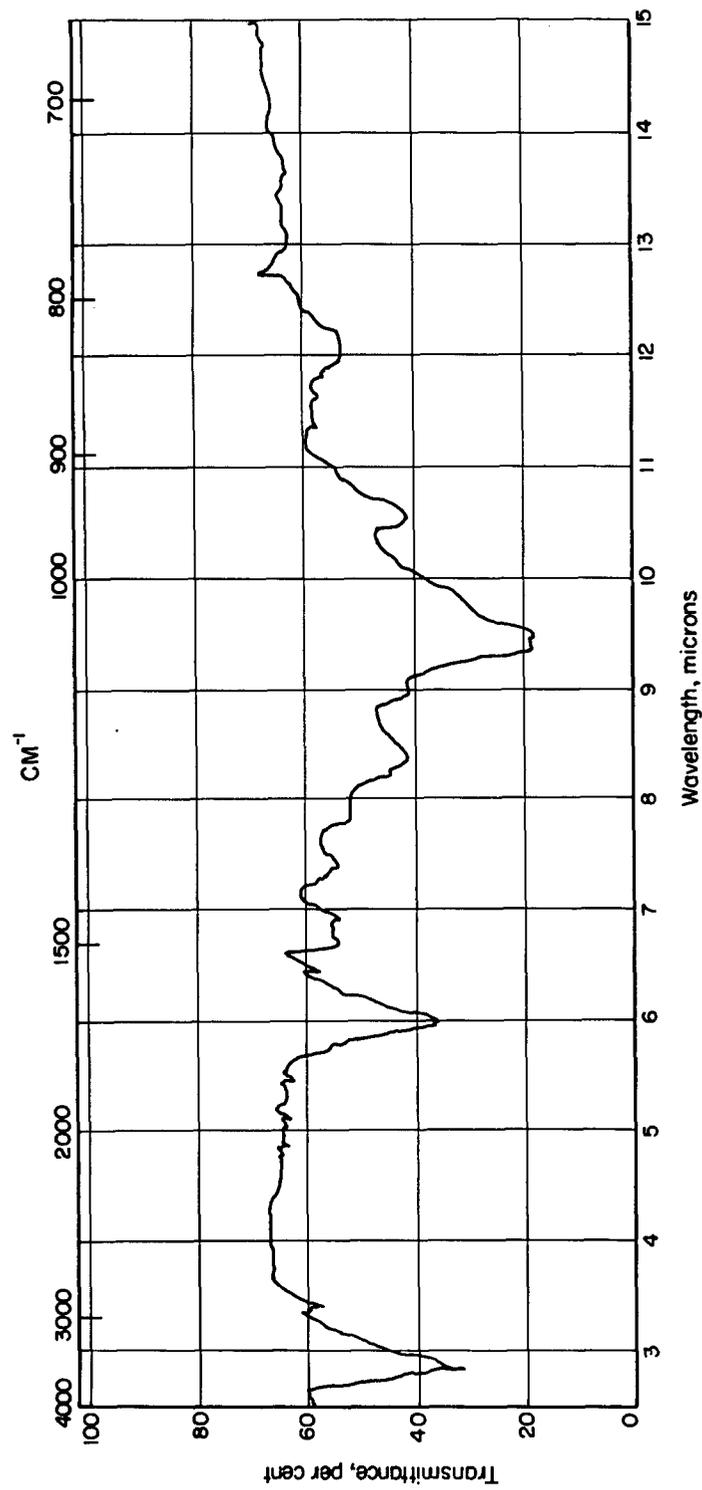


FIGURE 6. INFRARED SPECTRA OF SUBLIMATION-PURIFIED HIGH-PRESSURE HEATED PRODUCT OF QUINONE

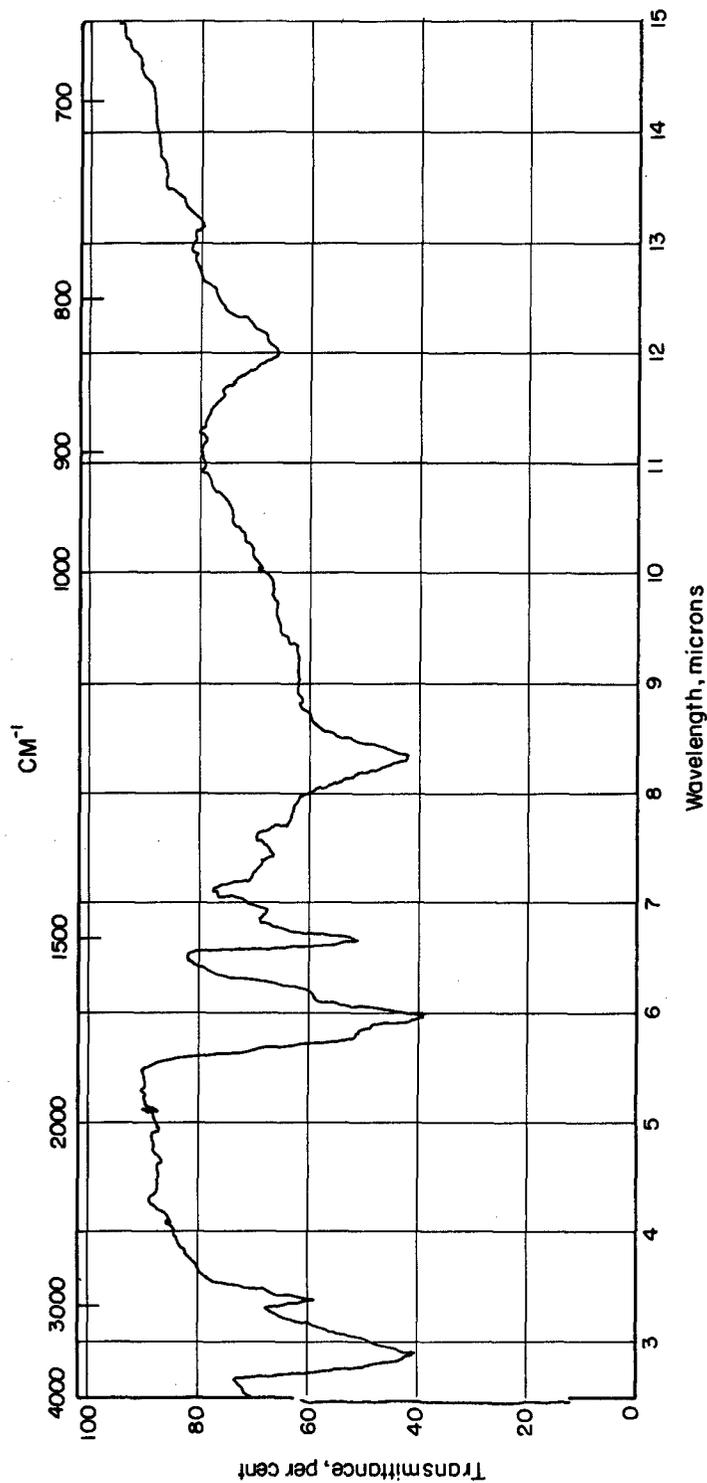


FIGURE 7. INFRARED SPECTRA OF SUBLIMATION-PURIFIED HIGH-PRESSURE PRODUCT OF QUINONE-METHYETHACRYLATE-BENZOYL PEROXIDE

Examination of the DTA thermograms on quinone and the unpurified compressed product (Figures 8 and 9, respectively) confirms that a significant change was produced through compression. Samples were admixed with aluminum oxide and heated at 10 C per minute under a blanket of nitrogen. Both samples show significant endothermic reactions around 100 C which are attributed to sublimation of residual quinone. This loss of sample results in a comparable base-line shift in both runs. There is no further significant pattern shown on the quinone thermogram since both analyses were conducted under extremely high sensitivity due to the small amount of sample used. The minor fluctuations in signal for both runs are attributed to instrument noise and changes in nitrogen-gas flow rate. Examination of the thermogram for the compressed material, Figure 10, shows that not all the product was sublimed and that an exothermic reaction occurs from 500 to 600 C. This appears to be due to oxidation of the remaining organic materials since an increase in nitrogen flow rate was shown to reduce the exotherm. Since a relatively low nitrogen flow rate was used to blanket the samples, it is believed that sufficient back-diffusion of oxygen occurred to oxidize the nonvolatile portion of the product.

Although infrared did not show a significant difference between the purified products from compressed quinone (19433-9) and the compressed quinone methylmethacrylate-benzoyl peroxide system (19433-26), differential thermal analysis of the unpurified products were quite different. Study of Figures 9 and 10 shows the following:

- (1) Considerable sublimable quinone remained in 19433-9.
- (2) Very little sublimable quinone was present in 19433-26.
- (3) The product from 19433-9 was thermally stable to around 500 C at which time oxidation started.
- (4) The product from 19433-26 showed a pronounced exotherm around 210 C.
- (5) Upon completion of the 210 C exotherm, the instrument returned to the base line and gave evidence of an oxidative reaction similar to the product from 19433-9.

The compression-induced reactivity was further verified by studying the solubility of the converted material. Small samples of the compression-treated materials were heated overnight in an oven at 212 F to volatilize unreacted quinone. Small samples of the residues after sublimation was placed in water, alcohol, and ether for 72 hours to determine whether any solubility would be manifested. No significant solubility was shown either by color in the solvent or by disappearance of the product. Quinone, run as a comparison, quickly dissolved to give a yellow solution.

In summary, work with nonmonomer systems has indicated that quinone is unique among the materials studied in that it possesses a pressure-induced reactivity. There appears to be a threshold pressure below which conversion is not affected. The reactivity appears to be sensitive to thermal conditions and catalysis. The product appears to have fair thermal stability and to be insoluble in common quinone solvents. Physical properties have not been highly defined nor have structural details been completely established.

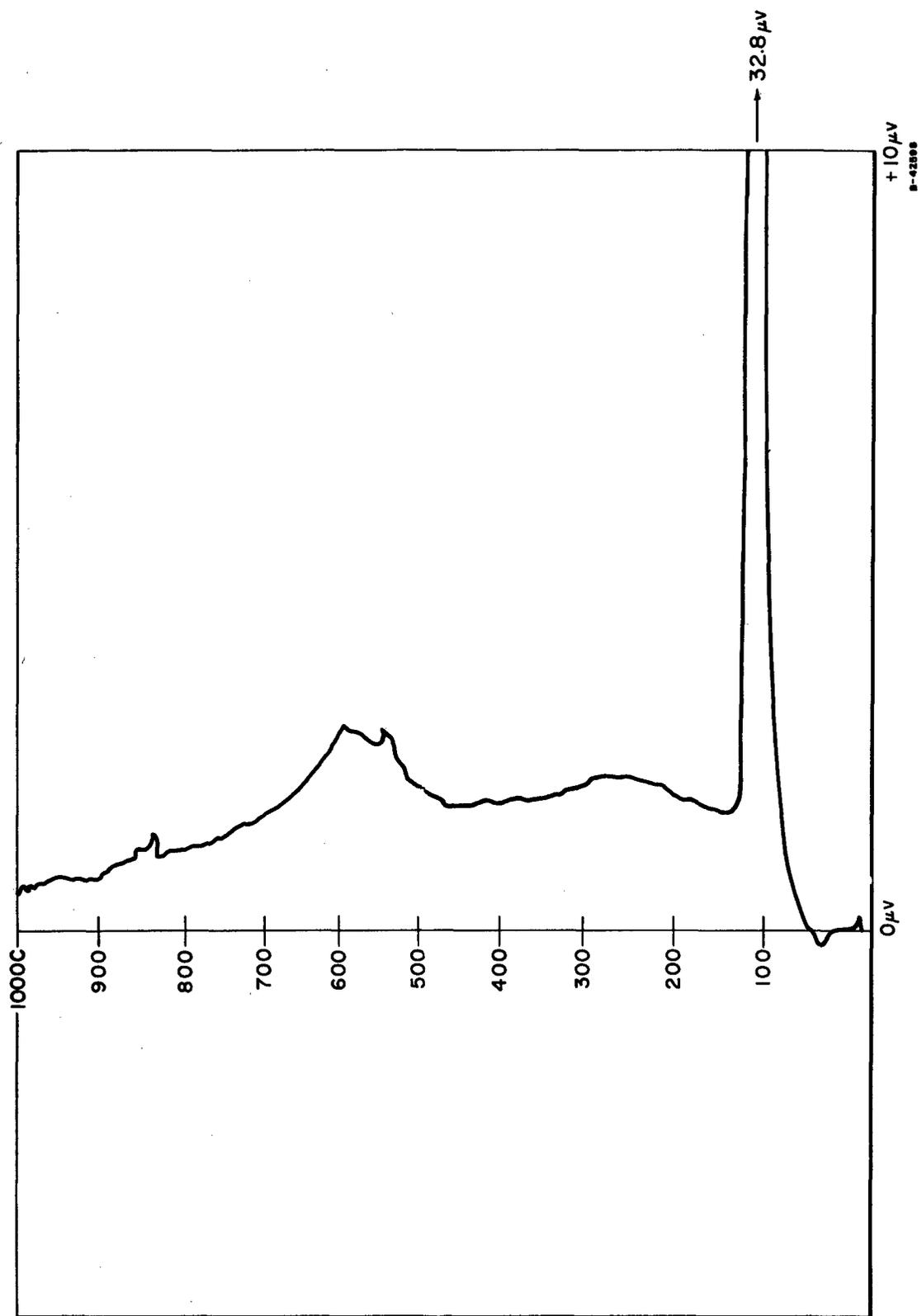


FIGURE 8. DIFFERENTIAL THERMAL ANALYSIS OF QUINONE

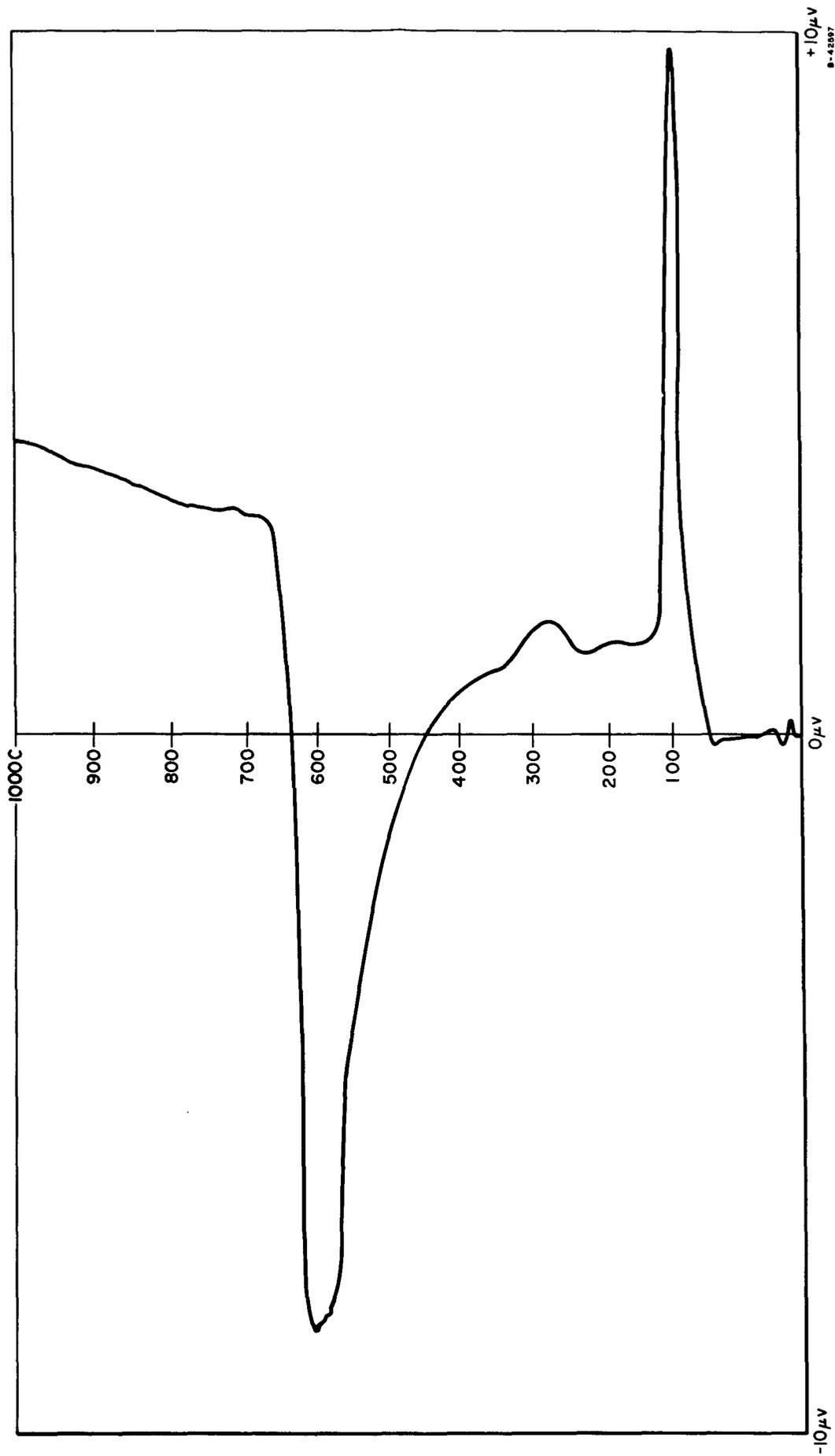


FIGURE 9. DIFFERENTIAL THERMAL ANALYSIS OF SUPERPRESSURE-TREATED QUINONE

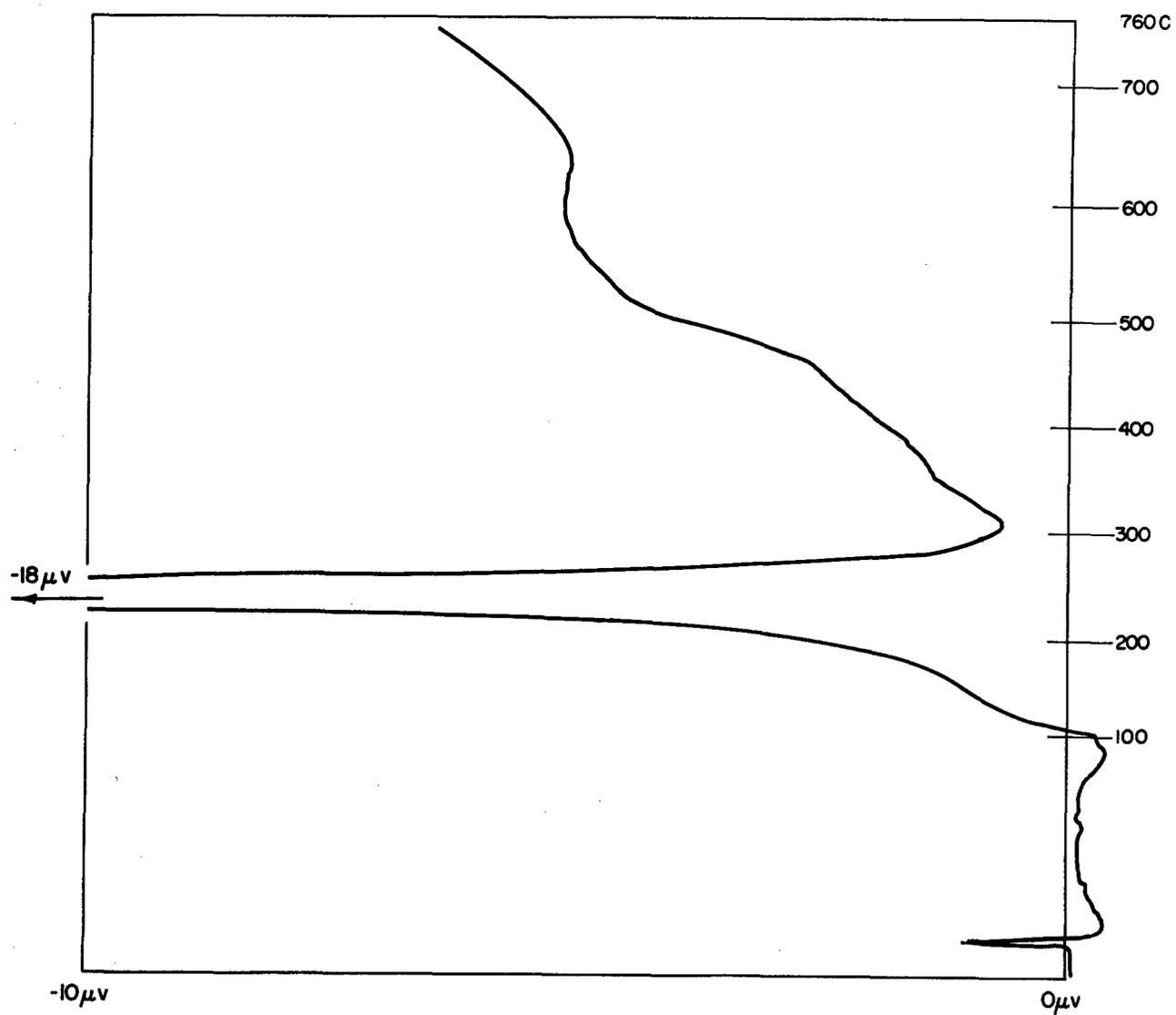


FIGURE 10. DIFFERENTIAL THERMAL ANALYSIS OF THE SUPERPRESSURE TREATED SYSTEM: QUINONE-METHYLMETHACRYLATE-BENZOYL PEROXIDE WITH HEAT

Analytical Methods

Evaluation of the effects of compression were generally simple observations of changes in appearance and state. These observations were augmented by density, durometer hardness, and melting-point determinations on appropriate samples. However, it was necessary to include more fundamental measurements on several products to better determine the structural changes during compression.

These techniques included infrared spectral measurements, differential thermal analysis, viscosity molecular weight, and molecular-weight distribution.

Infrared Analysis. Attempts to use Infracord measurements early in this program were discontinued when it was shown that changes in compressed polymers were not sufficient to show spectral differences in the microtomed film specimens. More recently, work with the nonmonomer compressions showed that considerable changes were effected in the compressed material and infrared studies proved valuable in confirming structural changes. Materials studied during this phase of the program generally were compressed powders. These were very amenable to the KBr pellet technique so this was used in obtaining the spectra presented in this report.

Differential Thermal Analysis. Powdered samples were admixed with aluminum oxide and heated at 10 C per minute under a blanket of nitrogen. Since very small amounts of sample were used, the runs were conducted under extremely high sensitivity with shifts as necessary to keep the pen on scale. This undoubtedly resulted in a greater amount of noise and base-line shift than would be encountered with a larger sample size. Normally a fixed standard nitrogen flow was used to blanket this operation. Momentary adjustments in flow, however, were used to verify trends shown on the thermogram. Thus evidence for an exothermic oxidation due to back-diffusing oxygen was strengthened by increasing the nitrogen flow to lessen the oxygen accessibility.

Viscosity Molecular-Weight Measurement. Although several methods are available for molecular-weight determination, it was believed that the viscosity technique would have the best over-all applicability. Such determinations are usually based on the empirical relationship $[\eta] = K M^a$ ⁽¹⁰⁾

where

$[\eta]$ is the viscosity extrapolated to zero concentration

K and a are constants for the polymer and solvent system

M is the molecular weight.

Viscosity data for a given system are obtained by accurately measuring and comparing the flow time of the solvent and solutions of known concentrations. In this instance the viscometer used was of the design by Schulken and Sparks⁽⁷⁾ (see Figure 11). Preliminary flow measurements in which the solute level was adjusted conventionally by aspiration showed an undesirable lack of reproduction. Investigation revealed that this spread in results, Figure 12, line C, was due to lack of satisfactory reproducibility in the back pressure as governed by the solution level.

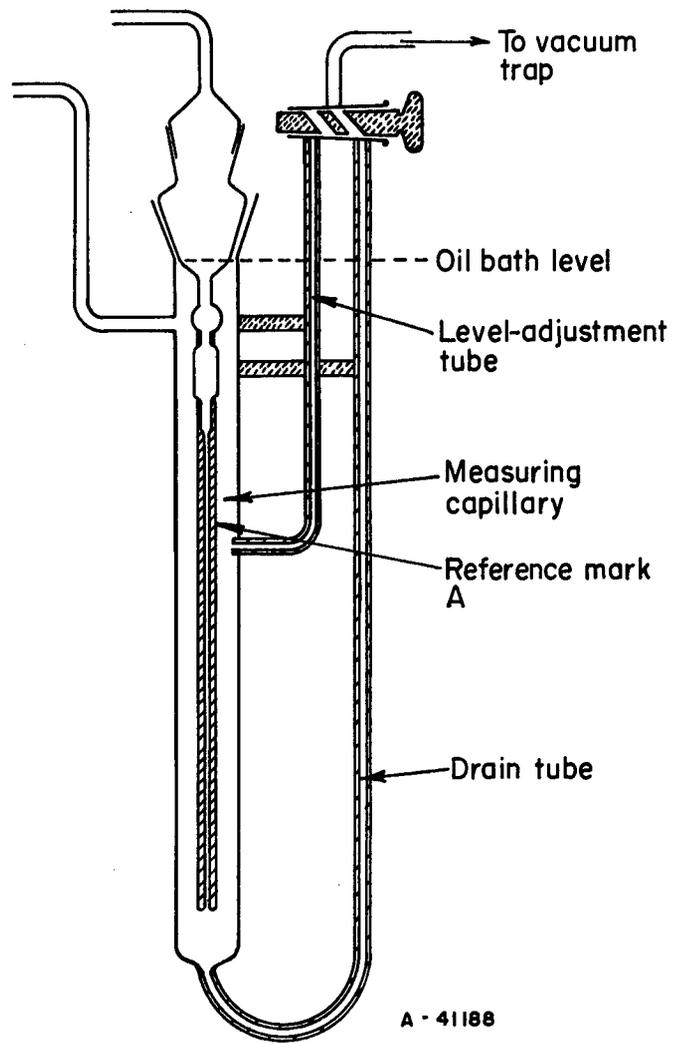


FIGURE 11. DIAGRAM OF SCHULKEN-SPARKS VISCOMETER.

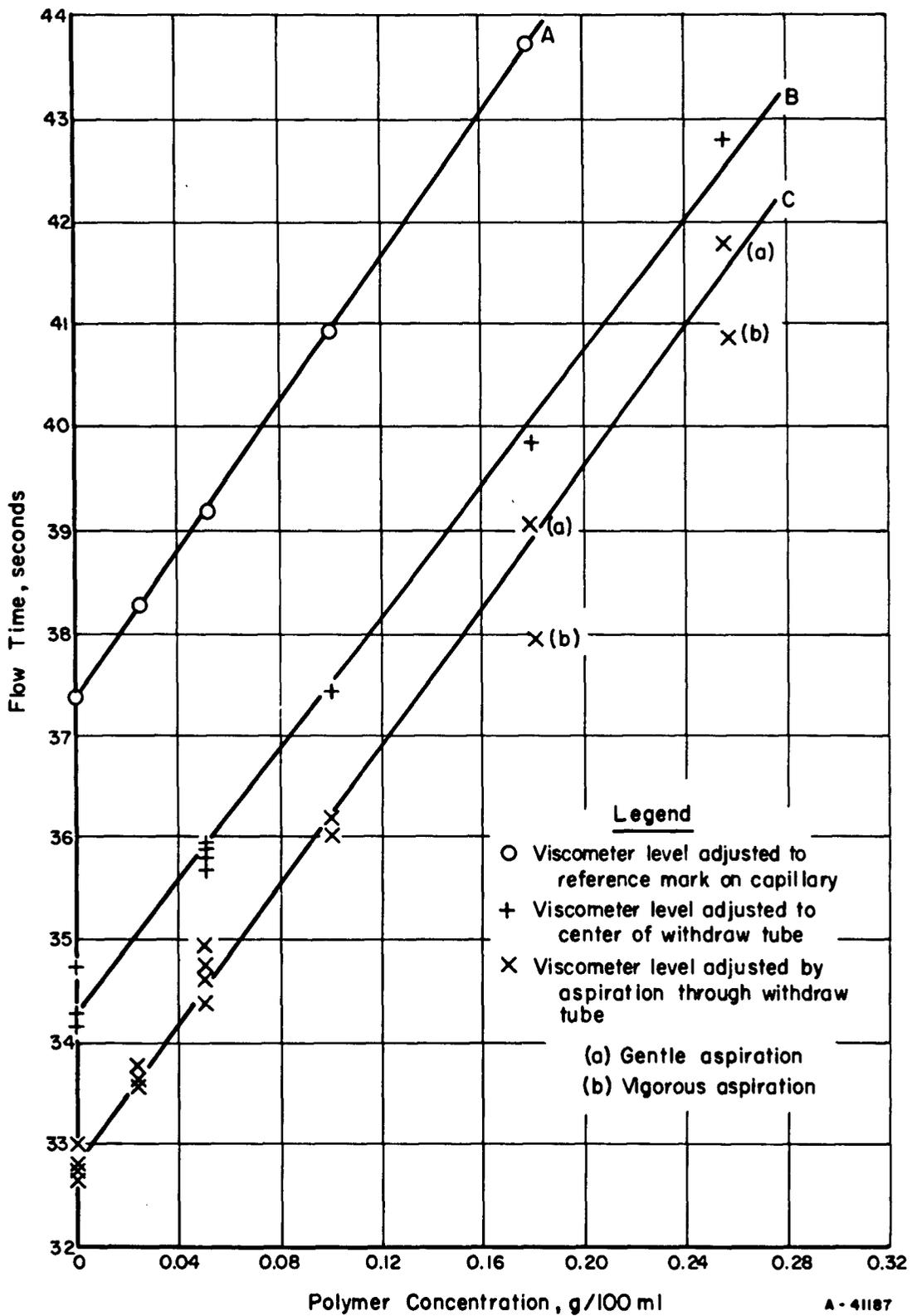


FIGURE 12. COMPARISON OF FLOW DATA FOR DIFFERENT VISCOMETER-LEVEL REFERENCE METHODS

The viscosity η is calculated from an equation of the form

$$\eta = \alpha \rho \left[t - \frac{\beta}{\alpha t} \right],$$

where

ρ is solution or solvent density

α and β are calibration constants in which β makes the correction for kinetic energy.

As the Shulkin and Sparks unit is designed to eliminate the kinetic-energy factor, this may be neglected so that the relative viscosity is equivalent to the solution flow time divided by the solvent flow time, since the α and ρ will cancel.

Molecular-Weight Distribution

Studies were made of the molecular-weight distribution of selected samples to determine whether significant changes occurred in the molecular spread. The method used for this study was the turbidimetric titration procedure of Morey and Tamblin.^(8,9) This method requires only a dilute solution of polymer, and is both rapid and sensitive in contrast to molecular-weight-distribution determinations by weight methods of separation. This procedure can be used for quantitative determination of molecular-weight distribution by calibration against known molecular-weight materials of the same type. For the purposes of the present study, the technique was used for comparison of the molecular weight of the compressed sample with that of a standard material. There are criticisms of this procedure when strict reliance is placed on it for quantitative evaluation of polymeric materials. However for indication of differences between samples of polymer such as are currently under study, this appeared to be a sensitive tool.

Essentially this method consists of running a precipitant into a dilute solution of polymer and measuring the turbidity of the solution due to precipitated polymer. Requirements for the procedure are that the solvent and precipitant are miscible in all proportions and that the precipitated polymer does not coagulate or settle out. Polymer concentrations of 0.01 per cent were used for these studies to give acceptable resolution on the Beckman DU spectrometer used for measuring turbidity. Coagulation was encountered in polycaprolactam precipitated from formic acid by water. This difficulty, however, was overcome by using water containing 0.1 per cent of an acid-stable wetting agent (Kreelon 8 D).

IV. EXPERIMENTAL SECTION - SEMIORGANIC POLYMERS

Introduction

A variety of semiorganic polymers have been prepared in recent years. In most of these materials a high degree of thermal stability has been obtained by avoiding

carbon-carbon bonds in the primary chain. The elements for such chains have been selected from various combinations of aluminum, boron, silicon, tin, or titanium alternating with less electropositive elements such as oxygen, sulfur, nitrogen, phosphorus, or arsenic. Preparation of polymers of this type having alkyl or aryl side chains has been accomplished by conventional reactions of organometallic compounds. Although polymers of moderately high molecular weight have been obtained, none of them combined all the desired properties of thermal stability, plasticity, and resistance to hydrolysis. Consequently, it is of value to investigate the possibility of using extreme pressure to achieve new polymerization reactions or modifications in known polymers that would result in improved properties.

The materials used in this program, with the exception of aluminum phenoxide, were all prepared previously, as described in Technical Documentary Report No. ASD-TDR-62-73. Those monomers and low polymers which offered the most promise of conversion to new products as a result of pressure were carried over from last year's program: (1) dimethyldicyanosilane, (2) four polyaluminosiloxanes, and (3) two arsenosiloxanes. In addition, the possibility of forming phthalocyanine polymers and polyaluminosiloxanes under ultrapressures was also investigated.

Apparatus and Techniques

For all of the pressurization experiments, the sample was enclosed in a platinum capsule 1/2 inch long and 1/16 inch in diameter. To form the capsule, a length of platinum tubing was held in a steel die while the bottom was sealed by tamping platinum foil into the base. The sample was then tamped into the capsule, and the top seal of platinum foil applied similarly. When the sample was to be heated beyond its melting point, the end seals were strengthened by sandwiching wadded foil between disks of platinum. For experiments at elevated temperatures, the platinum capsule served as a resistance heater.

For materials which are sensitive to oxygen or moisture, it was found necessary to load the capsules under a blanket of dry nitrogen or argon. Lamp-grade nitrogen proved to be suitable for this purpose in many cases, but for prolonged use of the "inert atmosphere box" the greater density of argon made it preferable. After pressure experiments with these sensitive materials, the capsules were opened in the inert atmosphere and the contents sealed in a vial under the same atmosphere for study of changes in properties and structure.

The pressurization experiments were carried out with both the belt and the girdle type of binding rings, pistons, and die. Experiments at 90,000 atm and above were carried out using the girdle equipment.

Pressurization Experiments

The materials which underwent a different reaction under ultrapressure from that which occurred on heating alone were studied under a variety of pressure-temperature combinations. In this way a reactivity diagram was constructed for each such material, delineating conditions of pressure and temperature at which reaction of some type occurs.

Dimethyldicyanosilane

Investigation of the temperature and pressure conditions under which $(\text{CH}_3)_2\text{Si}(\text{CN})_2$ undergoes reaction has revealed a possibly unique situation. The reactivity diagram, which is presented in Figure 13, shows that reaction occurs at lower temperatures as the pressure is increased. The zone of reactivity appears to be separated from the nonreactive zone by a straight line, whose position indicates that reaction is possible at room temperature if a pressure in the range 105,000 to 120,000 atmospheres is used. Polymerization has indeed been achieved by pressurization at 105,000 atmospheres at room temperature, although pyrolysis sometimes has occurred under these same conditions. When the pressure was increased to 115,000 atmospheres, only the pyrolytic reaction was obtained.

The products obtained when this compound reacts are quite different from the starting material. Dimethyldicyanosilane is a colorless crystalline solid which has a melting point of 81 to 83 C and is very sensitive to moisture and oxygen. When exposed to the atmosphere it changes within 2 minutes to a colorless oil having an infrared spectrum typical of silicones. However, the reaction product obtained in these experiments is a brown to black powder which does not melt, but decomposes slowly above 200 C. It is no longer reactive to moisture or oxygen, and it is insoluble in water and common organic solvents. These property changes are indicative of polymer formation. Unfortunately, the products obtained have been too insoluble to permit molecular-weight determination.

The infrared spectra of the original dimethyldicyanosilane and its reaction product are presented in Figure 14. In the reaction product, the absorption at 2.9 microns can be attributed to N-H bonding, and the band at 6.2 microns, to C = N. The C = N absorption at 4.6 microns has not been completely lost, although its intensity has been sharply reduced. A strong, broad band has appeared between 9 and 10 microns, and this absorption probably is the result of Si-O bonding.

Elemental analysis of these polymerized products for carbon, hydrogen, nitrogen, and silicon invariably accounts for approximately 80 per cent of the composition. In view of the infrared evidence, the remaining 20 per cent may be attributed to oxygen. Experiments in which contact with the atmosphere was prevented during loading and unloading of the press have demonstrated that very little reaction occurs when the system is pressurized under these circumstances. Since there is also an increase in the H/Si ratio in the products, it is probable that water vapor takes part in the reaction.

A comparison of the analyses of the starting $(\text{CH}_3)_2\text{Si}(\text{CN})_2$ and a typical reaction product is presented in the tabulation below.

	<u>Weight Per Cent of Element</u>			
	<u>C</u>	<u>H</u>	<u>N</u>	<u>Si</u>
Theoretical	43.6	5.4	25.5	25.5
Starting Material	43.1	5.8	23.4	25.4
Reaction Product	36.3	6.1	17.9	18.7

The low nitrogen in the starting material is believed to be due to some hydrolysis which was observed during handling of the sample. The analysis of the reaction product accounts for only 79.0 per cent of the sample, and the remaining 21.0 per cent can be attributed to oxygen.

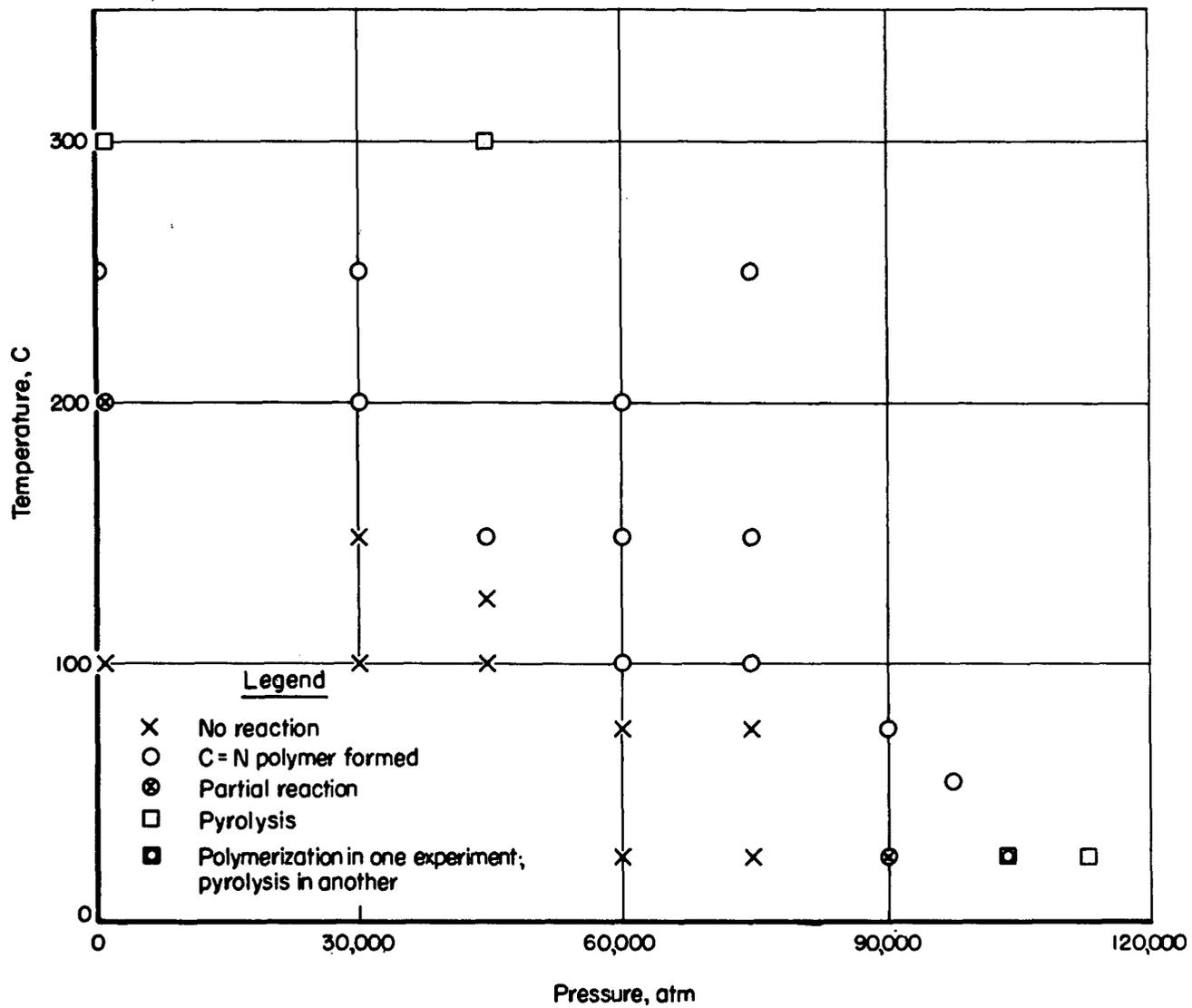


FIGURE 13. EFFECT OF PRESSURE AND TEMPERATURE ON REACTIVITY OF DIMETHYLDICYANOSILANE

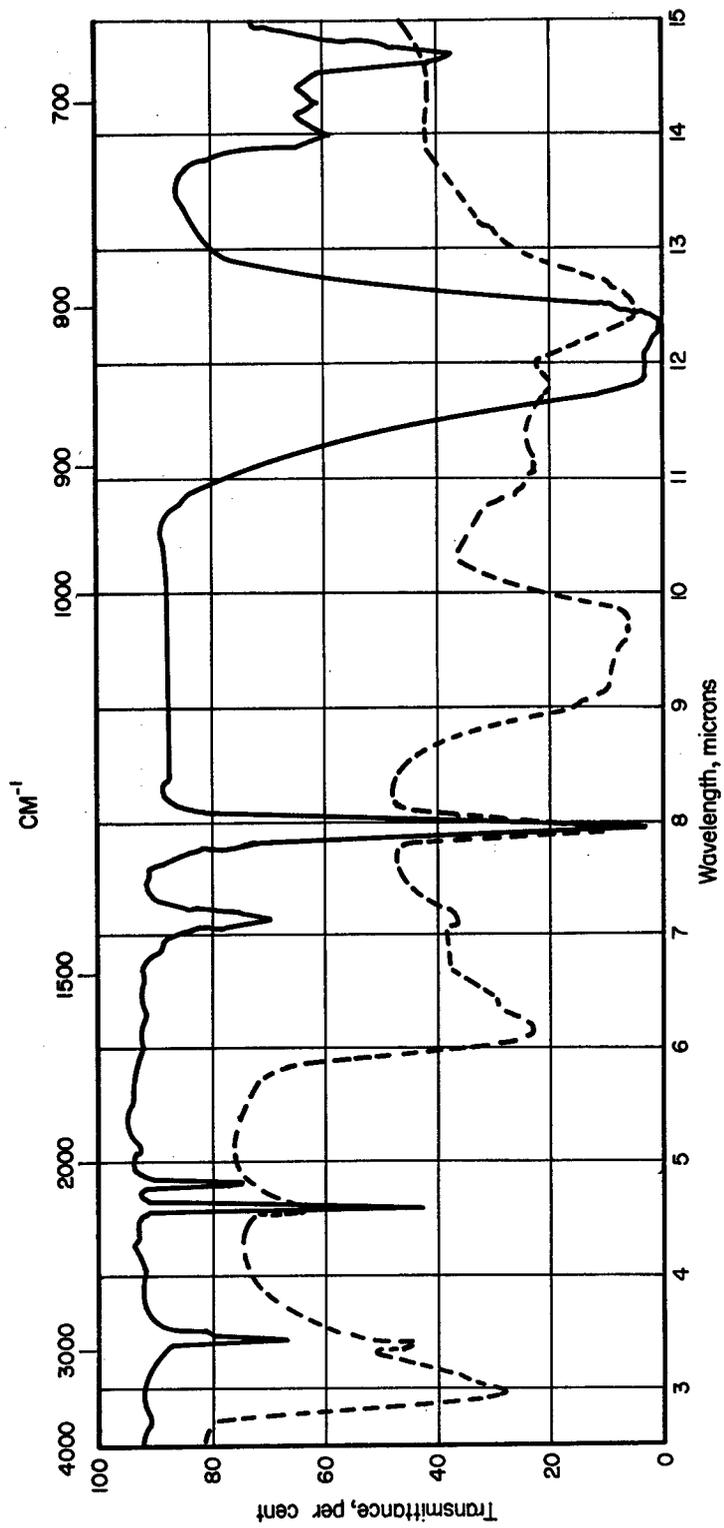
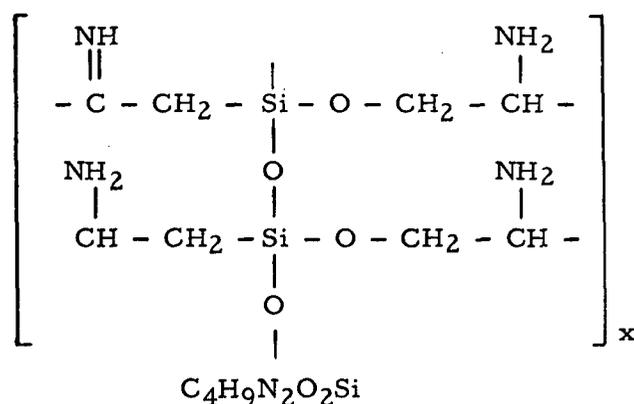


FIGURE 14. INFRARED SPECTRA OF DIMETHYLDICYANOSILANE (SOLID LINE) AND ITS HIGH-PRESSURE REACTION PRODUCT (BROKEN LINE)

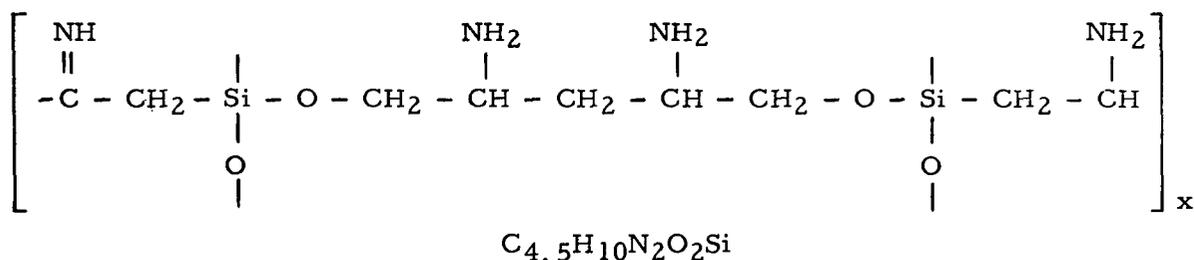
The polymeric reaction products obtained under different conditions of temperature and pressure are not identical in composition, although they do have similar infrared absorption spectra. Elemental analysis of three products obtained by reaction at different pressures and 250 C shows distinct differences in composition. The atom ratios of these products compare with those of the starting material as follows:

Pressure, atm	Atom Ratio			
	C/Si	H/Si	N/Si	O/Si
0-1	6	11	3	2
30,000	4.5	10	2	2
75,000	4	9	2	2
Starting Material	4	6	2	0

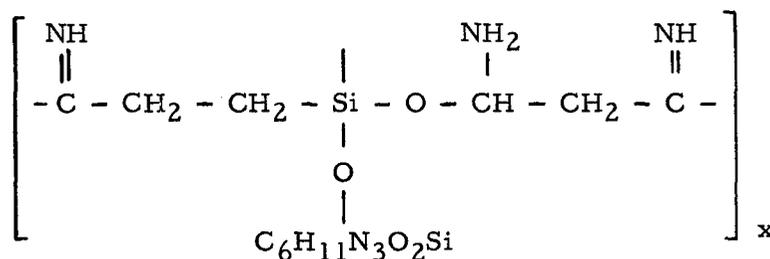
These results indicate that the configuration of the original material is maintained more closely during polymerization under the higher pressures. Structures can be postulated that fit the experimental data for the products obtained under these different conditions. The following structure is proposed for the material which results at 75,000 atm:



An increase in both the C/Si and H/Si atom ratios was found in the product which was obtained at 30,000 atm. This result can be accounted for by the structure:



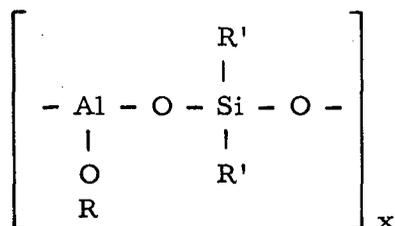
The product obtained when the dimethyldicyanosilane is heated in a sealed tube under its own vapor pressure shows an increase in all the atom ratios, indicating that extensive rearrangement has occurred, resulting in a structure such as:



The weak C = N infrared absorption band that remains in the reaction products is possibly due to end groups of such chains.

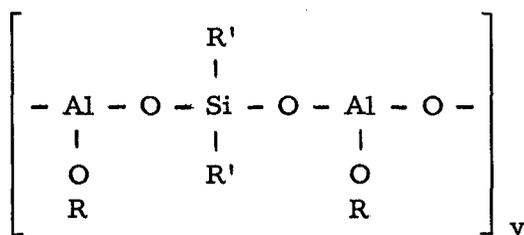
Polyaluminosiloxanes

These materials are low polymers having the structure:



The preparations used in this study included acetylacetone and isopropoxide (as the OR bonded to the aluminum) and methyl, ethyl, or phenyl (as R' attached to silicon).

However, for the material in which R' is methyl and OR is chelated acetylacetone, a 2 to 1 ratio of aluminum to silicon was indicated by elemental analysis. This result could be explained by postulating the structure:



If y in the above structure is 2, and the end groups are acetylacetone and isopropyl, both of which were employed in the preparation, the calculated molecular weight is 874. A molecular-weight determination was made on the material by elevation of the boiling point of benzene, using a Menzies-Wright differential water thermometer. A value of 867 was obtained by this technique.

The effect of various combinations of pressure and temperature on this material is shown in Figure 15. Pressure has an inhibiting effect on reactivity, as indicated in the plot. In addition, the reaction occurring under ultrahigh pressure is different from that found at 1 atmosphere, although in both cases the product is less soluble and has greater thermal stability, indicating some further polymerization.

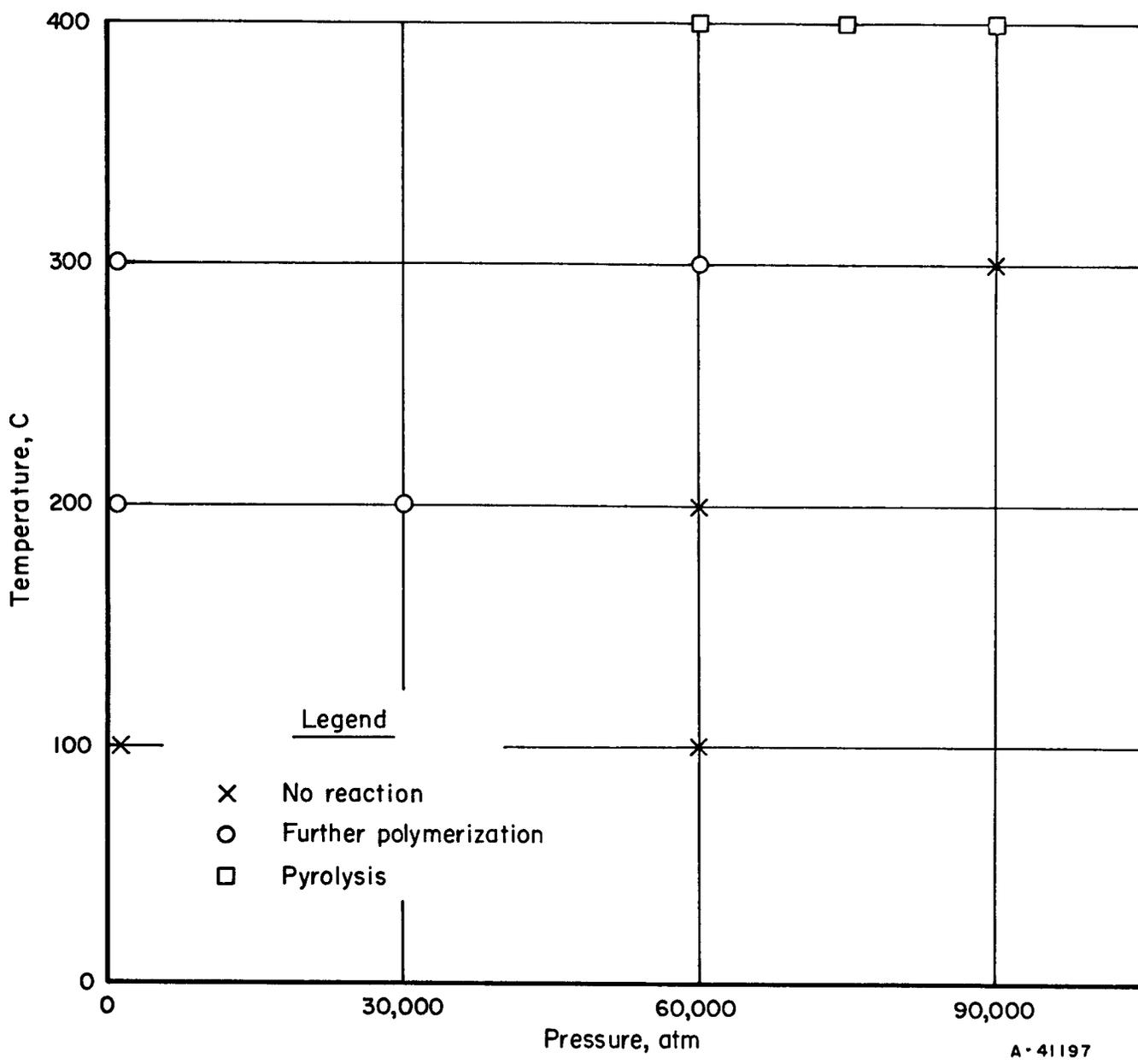


FIGURE 15. EFFECT OF PRESSURE AND TEMPERATURE ON THE DIMETHYLSILOXY-ALUMINUM-ACETYLACETONATE POLYMER

The amount of silicon-methyl bonding is sharply reduced in the extreme-pressure product, as shown by decreased absorptions at 7.95 and 12.5 microns in the infrared spectrum (Figure 16). At the same time there is an increase in the amount of OH bonding (2.9 microns), probably at the sites where the methyl groups are lost. On the other hand, the product of reaction at 1 atmosphere shows no loss of methyl groups, but rather a rearrangement in the acetylacetonate portion of the molecule.

The thermogravimetric curves (*in vacuo*) for the starting material and the products resulting from (1) pressurizing at 60,000 atmospheres and 300 C and (2) heating in an evacuated, sealed tube at 300 C are given in Figure 17. An appreciable increase in thermal stability is shown in the pressurized product above 100 C, although it contains a larger fraction of material volatilizing below 100 C. This difference may be related to the increase in OH bonding observed for the reaction product. Such groups may split out water when heated to 100 C in a vacuum. The unpressurized product obtained at 300 C displays a thermal stability which is better than that of the starting material, but not so good as that of the pressurized product. This difference probably results from a larger amount of crosslinking in the pressurized product.

The reactivity plot for the aluminosiloxane in which R' is ethyl and OR is acetylacetonate is presented in Figure 18. The nature of the high-pressure reaction is the same as for the methyl derivative, resulting in breaking of Si-C bonds and formation of additional OH bonds at 60,000 atmospheres. At 1 atmosphere, rearrangement of the acetylacetonate ring occurs at 300 C.

The infrared spectra shown in Figure 19 indicate less difference between starting material and product than was observed for the corresponding methyl derivative. This effect is also noticed when the products obtained at 30,000 atmospheres and 200 C are compared. For the methyl derivative, the infrared spectrum of the product resembles that obtained at 60,000 atmospheres rather than the one obtained in a sealed-tube reaction. Just the reverse is true in the case of the ethyl derivative. The thermogravimetric curves presented in Figure 20 show that an appreciable increase in stability results from pressurization of the sample at 60,000 atmospheres and 300 C. Again, the unpressurized product obtained at 300 C has an intermediate thermal stability.

For the material in which R' is ethyl and OR is isopropoxide, the typical behavior under pressure is noted. Silicon-carbon bonds are broken when reaction occurs at 60,000 atmospheres, whereas the isopropoxide group alone is affected by reaction at 1 atmosphere (Figures 21 and 22). An important difference from the materials having acetylacetonate chelated to the aluminum is that, at 350 C, higher pressures (even up to 90,000 atmospheres) do not prevent the breaking of silicon-carbon bonds. The thermogravimetric data shown in Figure 23 bear out the fact that not much thermal stability is gained by pressurizing this material.

In the case where isopropoxide is bonded to aluminum, and phenyl is on the silicon, the initiation of reaction is noted at only 100 C when the pressure is 60,000 atmospheres, and pyrolysis occurs at 300 C (Figures 24 and 25). Loss of $-CH_3$ from the isopropoxide is indicated by the infrared spectrum, together with some substitutional changes on the phenyl rings, and increase of OH bonding. Another difference from previously discussed materials is the prevention of the pyrolysis by increasing the pressure to 75,000 atmospheres. The thermogravimetric curves which are shown in Figure 26 show that little difference in thermal stability exists among the starting material, the pressurized

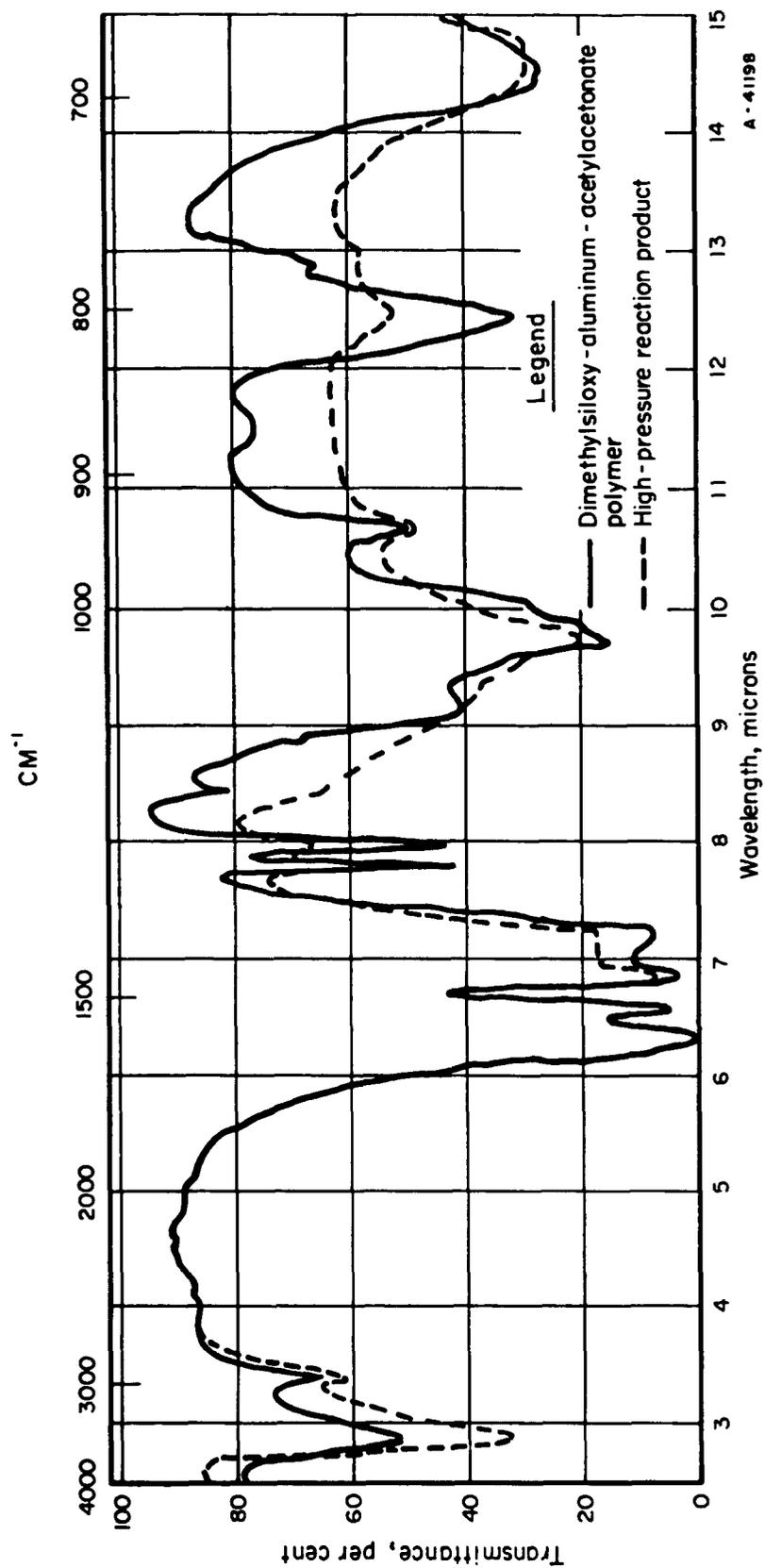


FIGURE 16. INFRARED SPECTRA OF DIMETHYLSILOXY-ALUMINUM-ACETYLACETONATE POLYMER AND ITS HIGH-PRESSURE REACTION PRODUCT

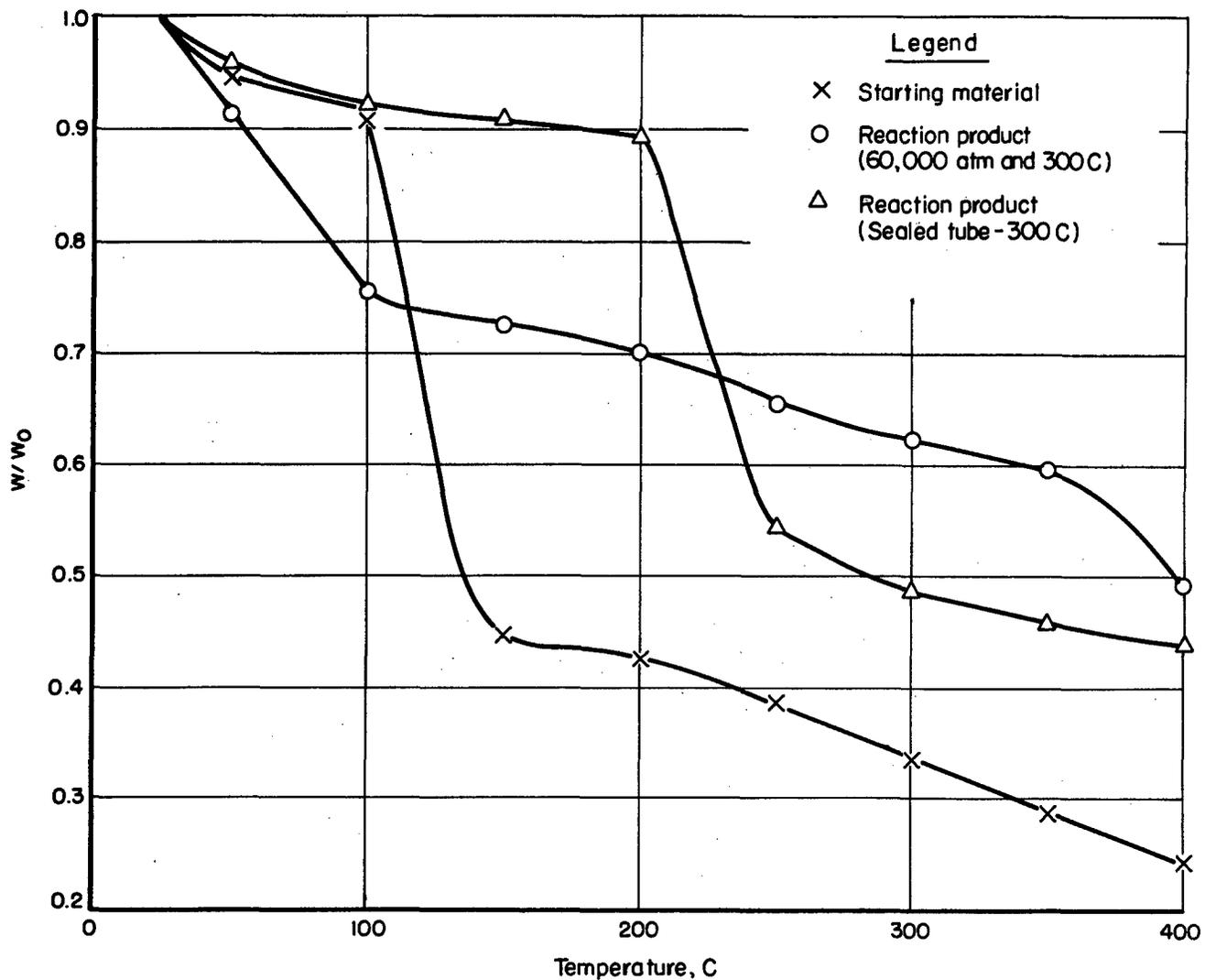
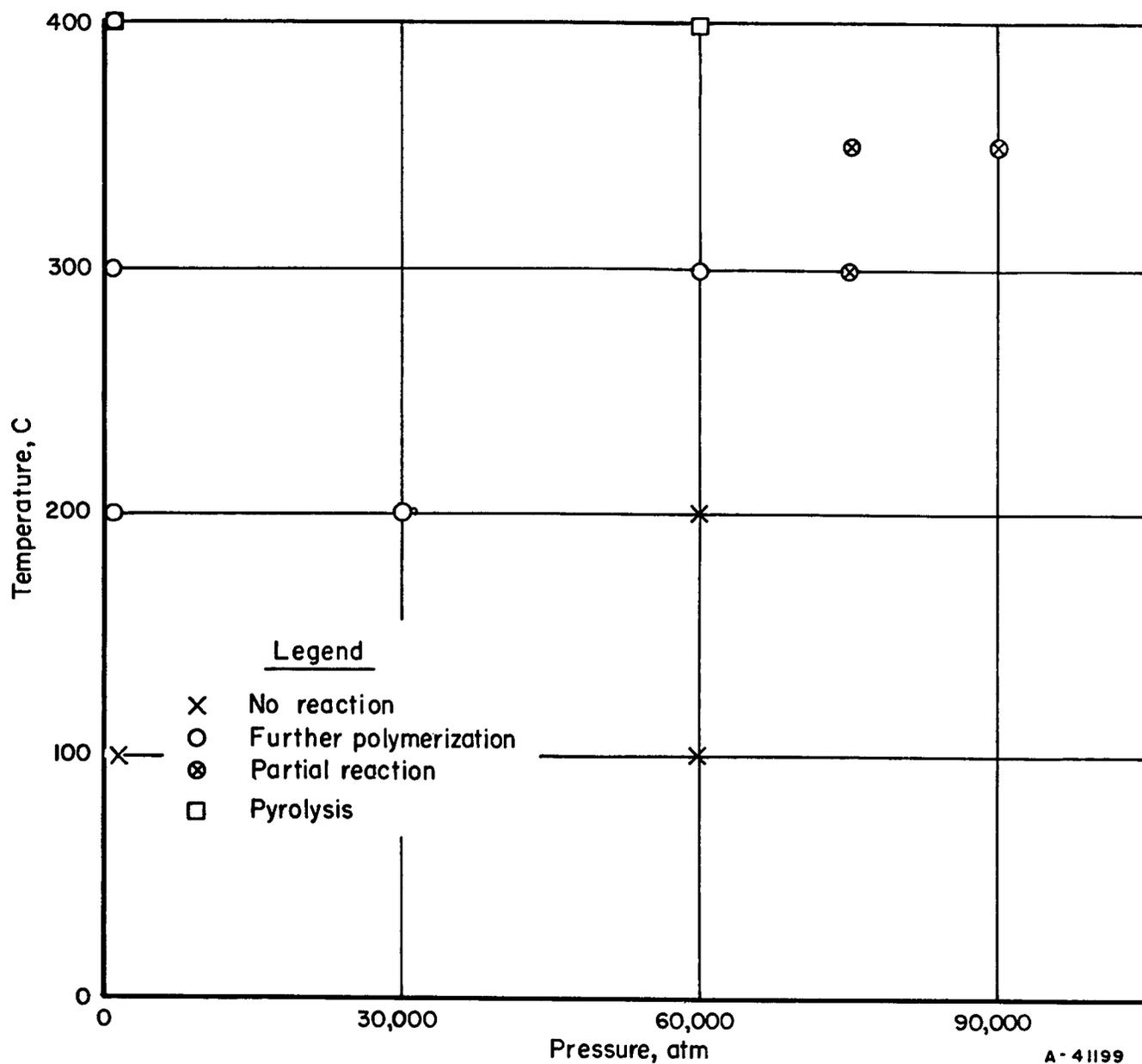


FIGURE 17. THERMOGRAVIMETRIC CURVES FOR THE DIMETHYLSILOXY-ALUMINUM-ACETYLACETONATE POLYMER AND ITS PRESSURIZED AND UNPRESSURIZED REACTION PRODUCTS



A-41199

FIGURE 18. EFFECT OF PRESSURE AND TEMPERATURE ON THE DIETHYLSILOXY-ALUMINUM-ACETYLACETONATE POLYMER

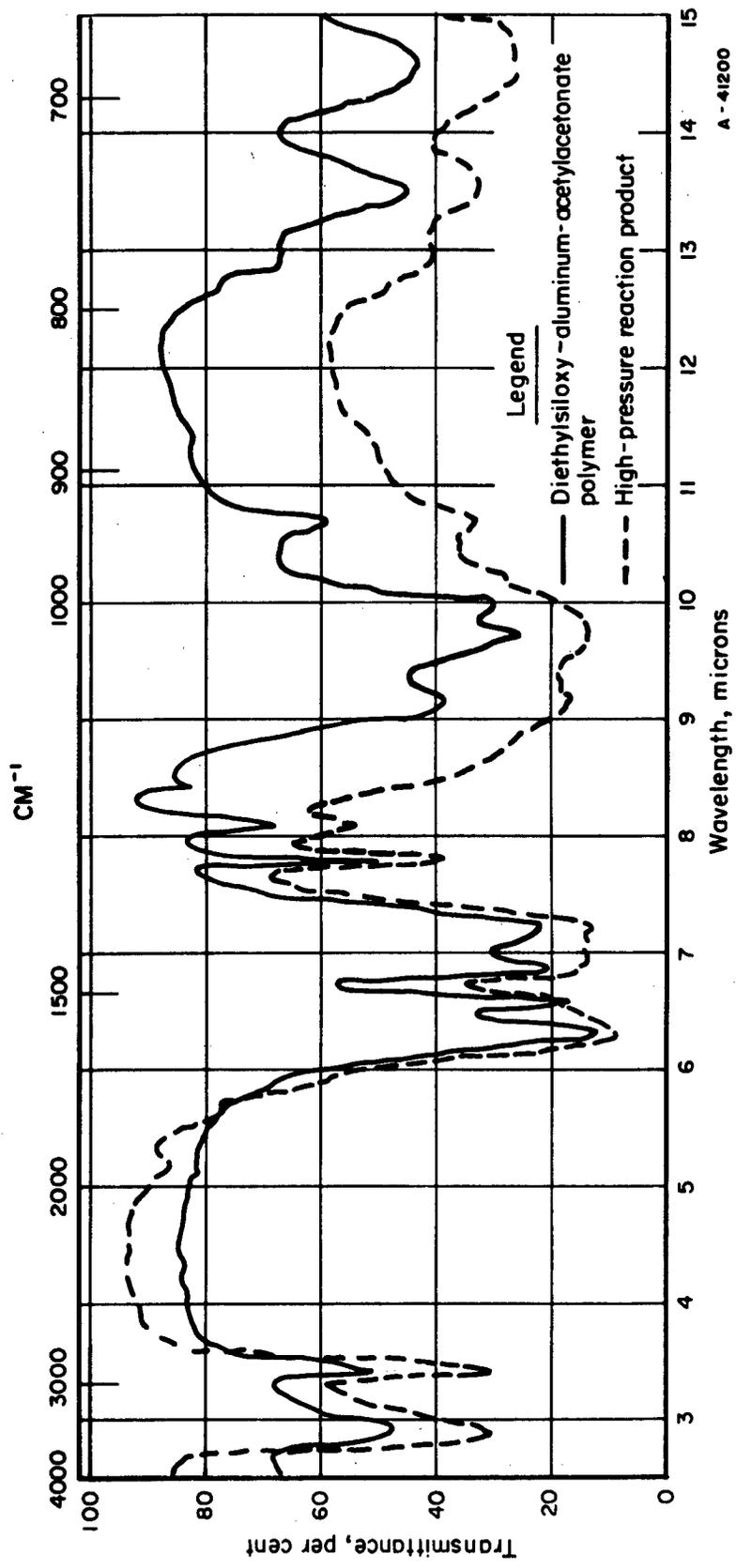


FIGURE 19. INFRARED SPECTRA OF DIETHYLSILOXY-ALUMINUM-ACETYLACETONATE POLYMER AND ITS HIGH-PRESSURE REACTION PRODUCT

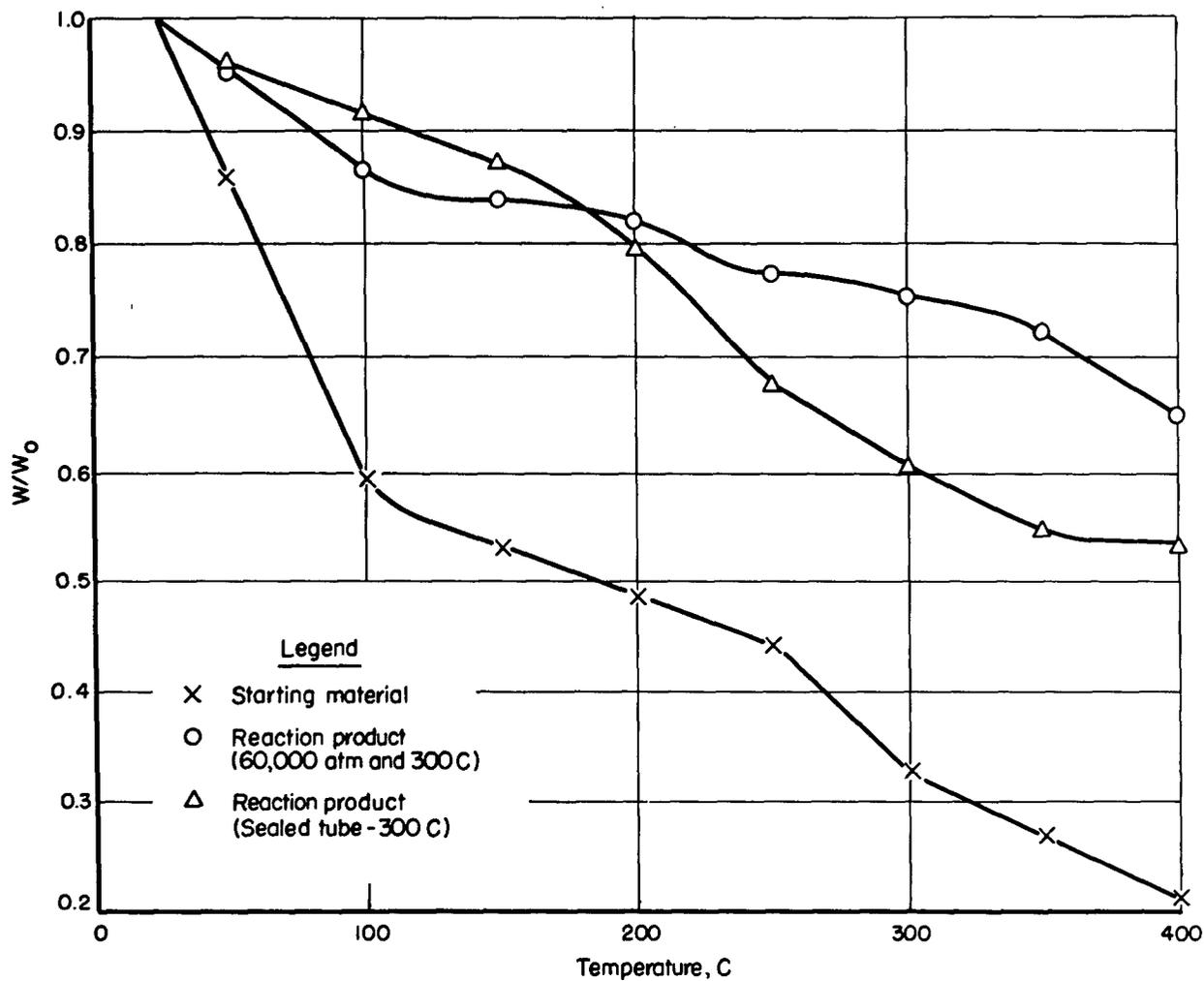
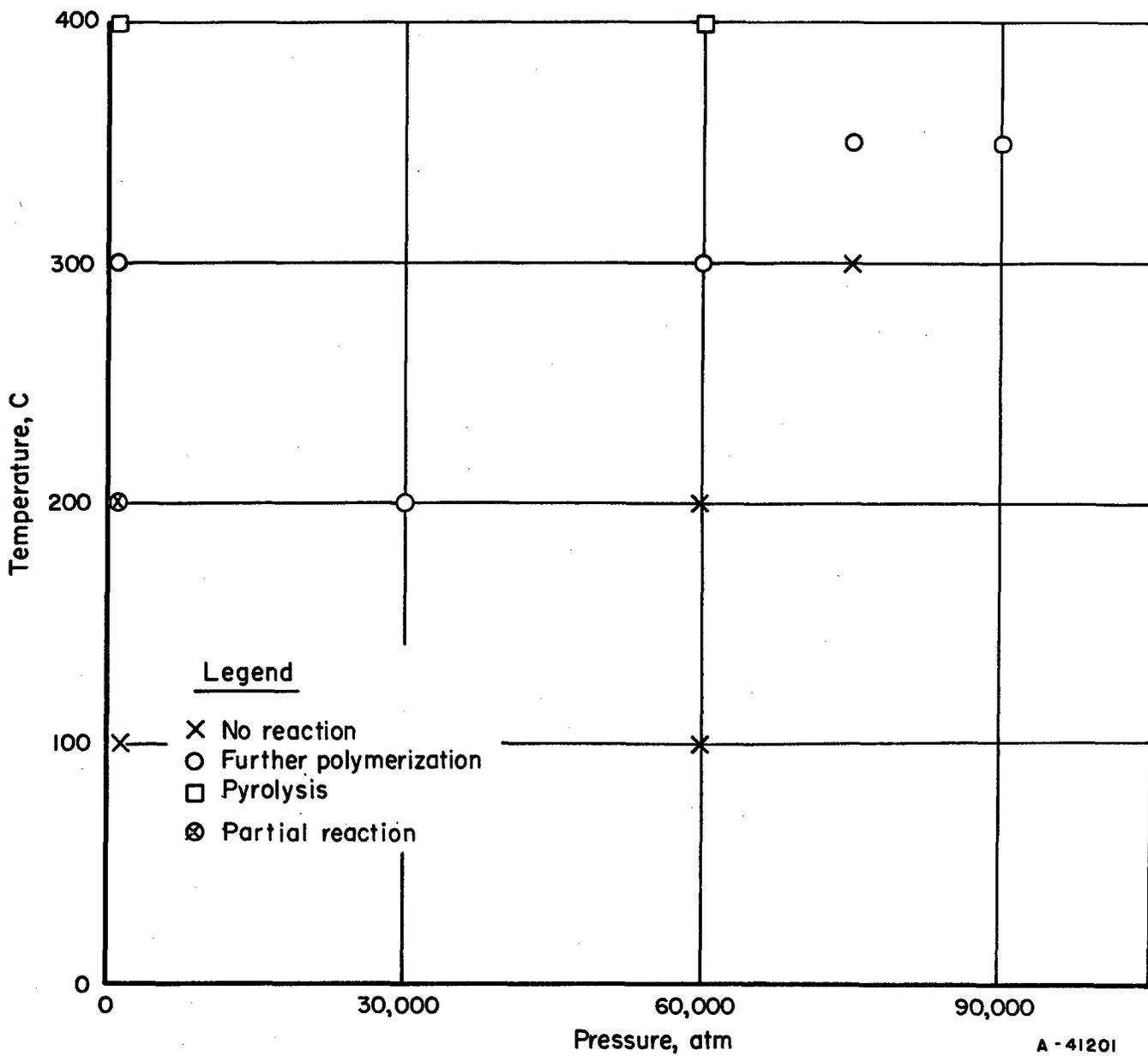
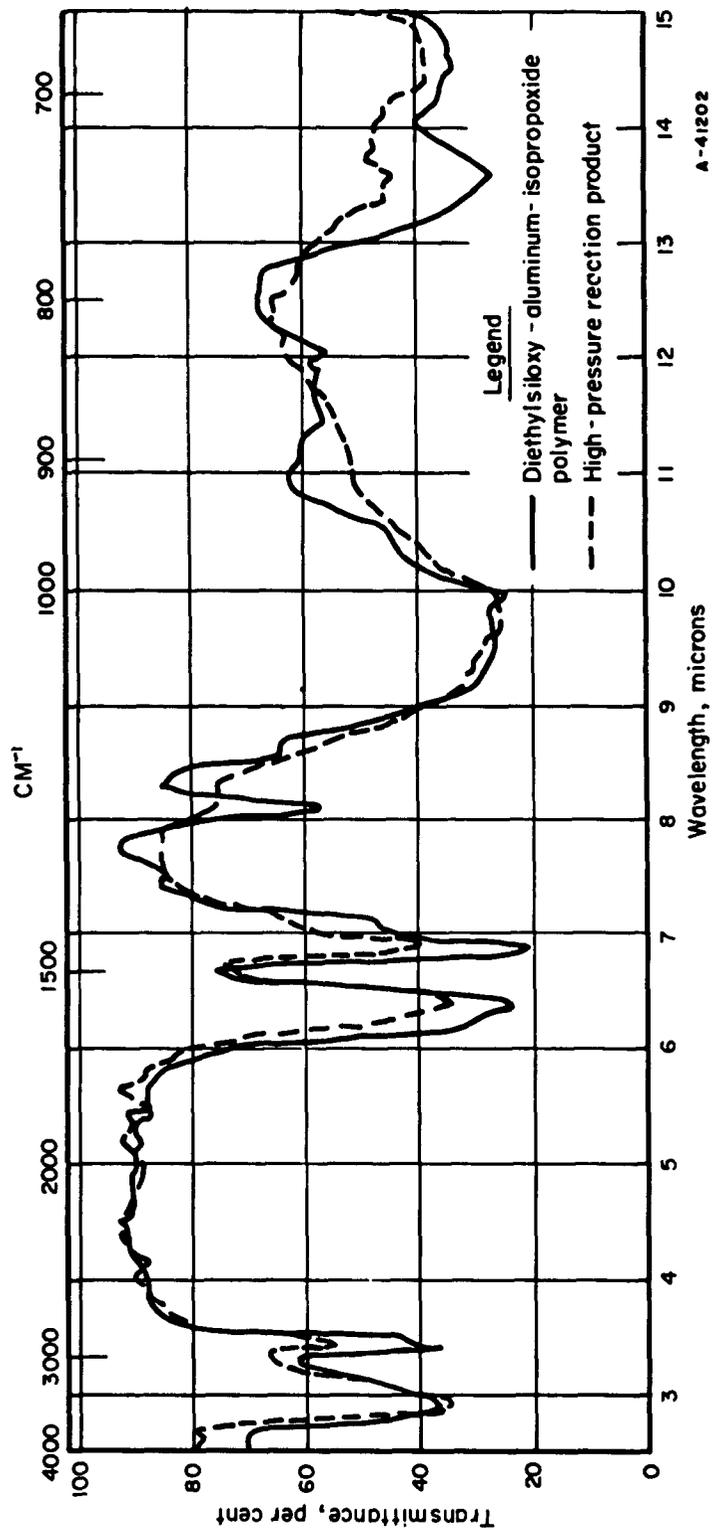


FIGURE 20. THERMOGRAVIMETRIC CURVES FOR THE DIETHYLSILOXY-ALUMINUM-ACETYLACETONATE POLYMER AND ITS PRESSURIZED AND UNPRESSURIZED REACTION PRODUCTS



A-41201

FIGURE 21. EFFECT OF PRESSURE AND TEMPERATURE ON THE DIETHYLSILOXY-ALUMINUM-ISOPROPOXIDE POLYMER



A-41202

FIGURE 22. INFRARED SPECTRA OF DIETHYLSILOXY-ALUMINUM-ISOPROPOXIDE POLYMER AND ITS HIGH-PRESSURE REACTION PRODUCT

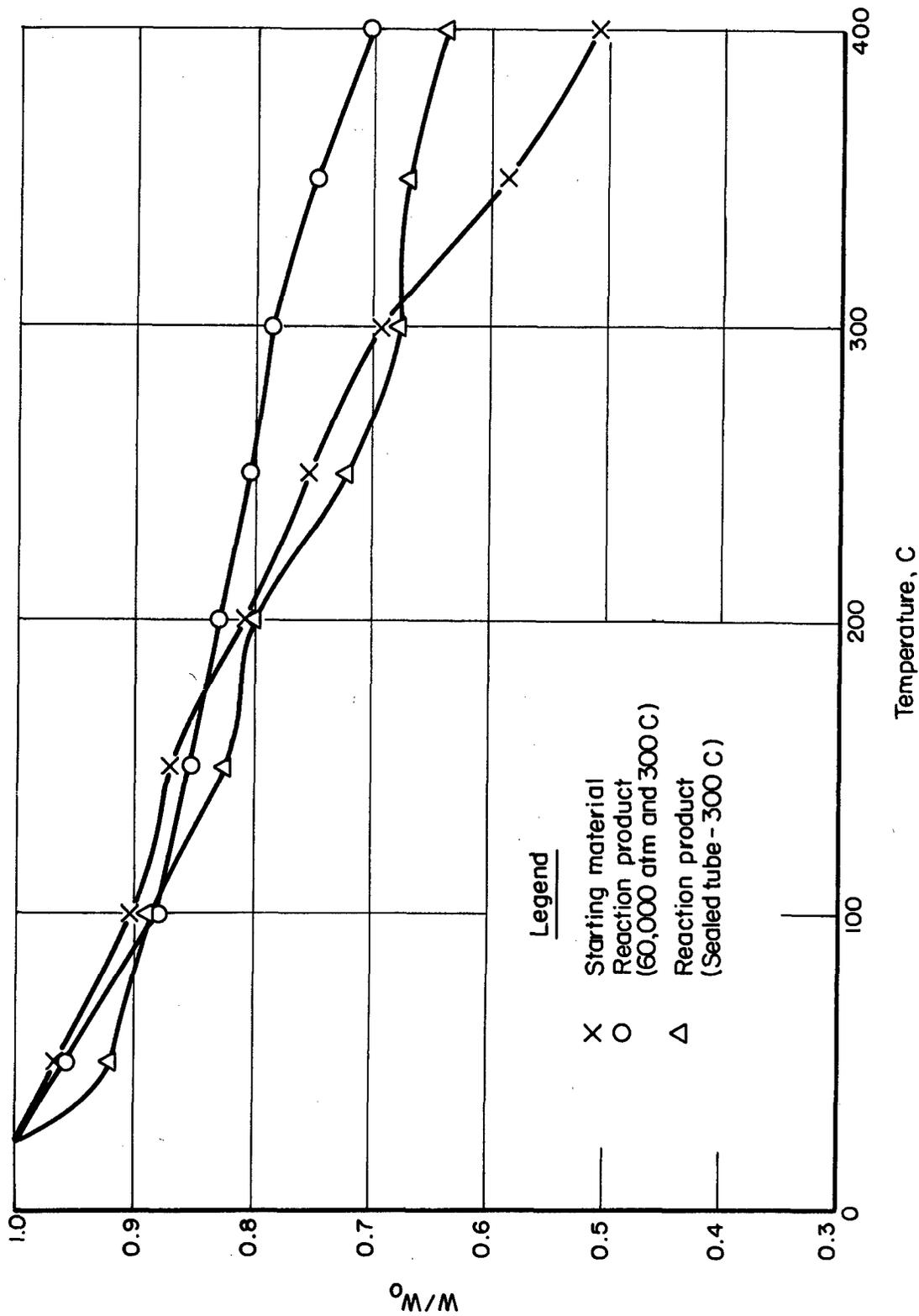


FIGURE 23. THERMOGRAVIMETRIC CURVES FOR THE DIETHYLSILOXY-ALUMINUM-ISOPROPOXIDE POLYMER AND ITS PRESSURIZED AND UNPRESSURIZED REACTION PRODUCTS

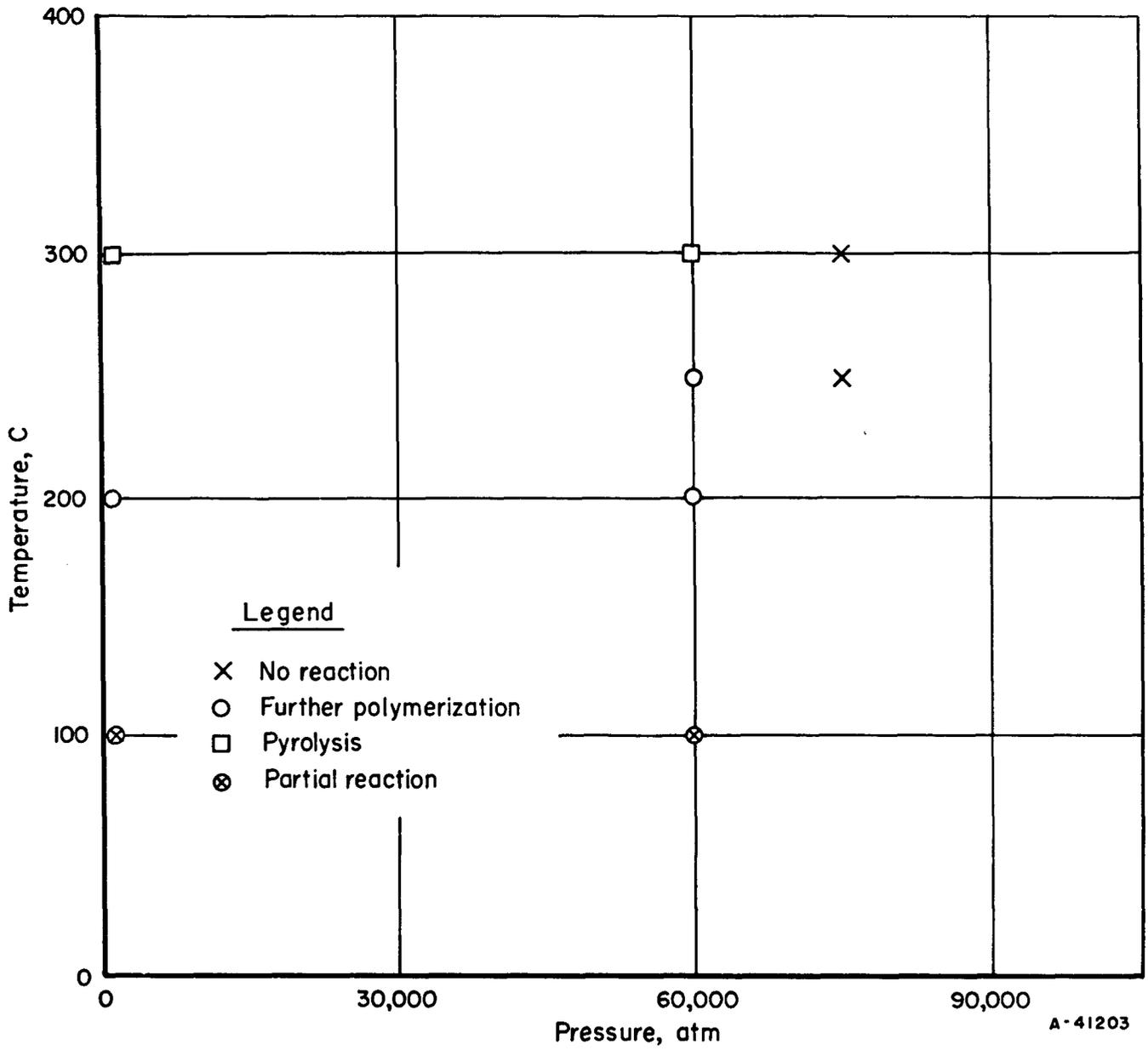


FIGURE 24. EFFECT OF PRESSURE AND TEMPERATURE ON THE DIPHENYLSILOXY-ALUMINUM-ISOPROPOXIDE POLYMER

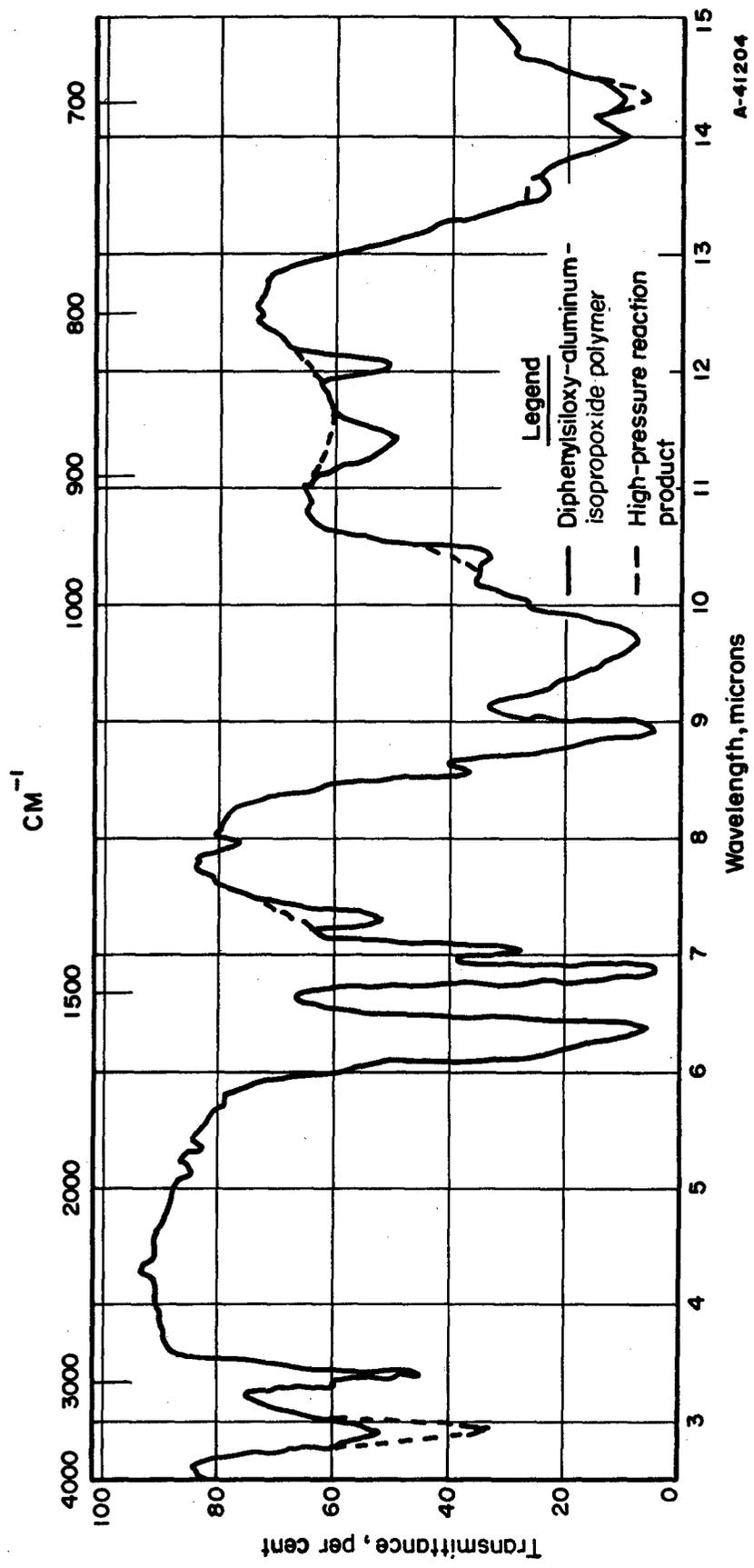


FIGURE 25. INFRARED SPECTRA OF DIPHENYLSILOXY-ALUMINUM-ISOPROPOXIDE POLYMER AND ITS HIGH-PRESSURE REACTION PRODUCT

A-41204

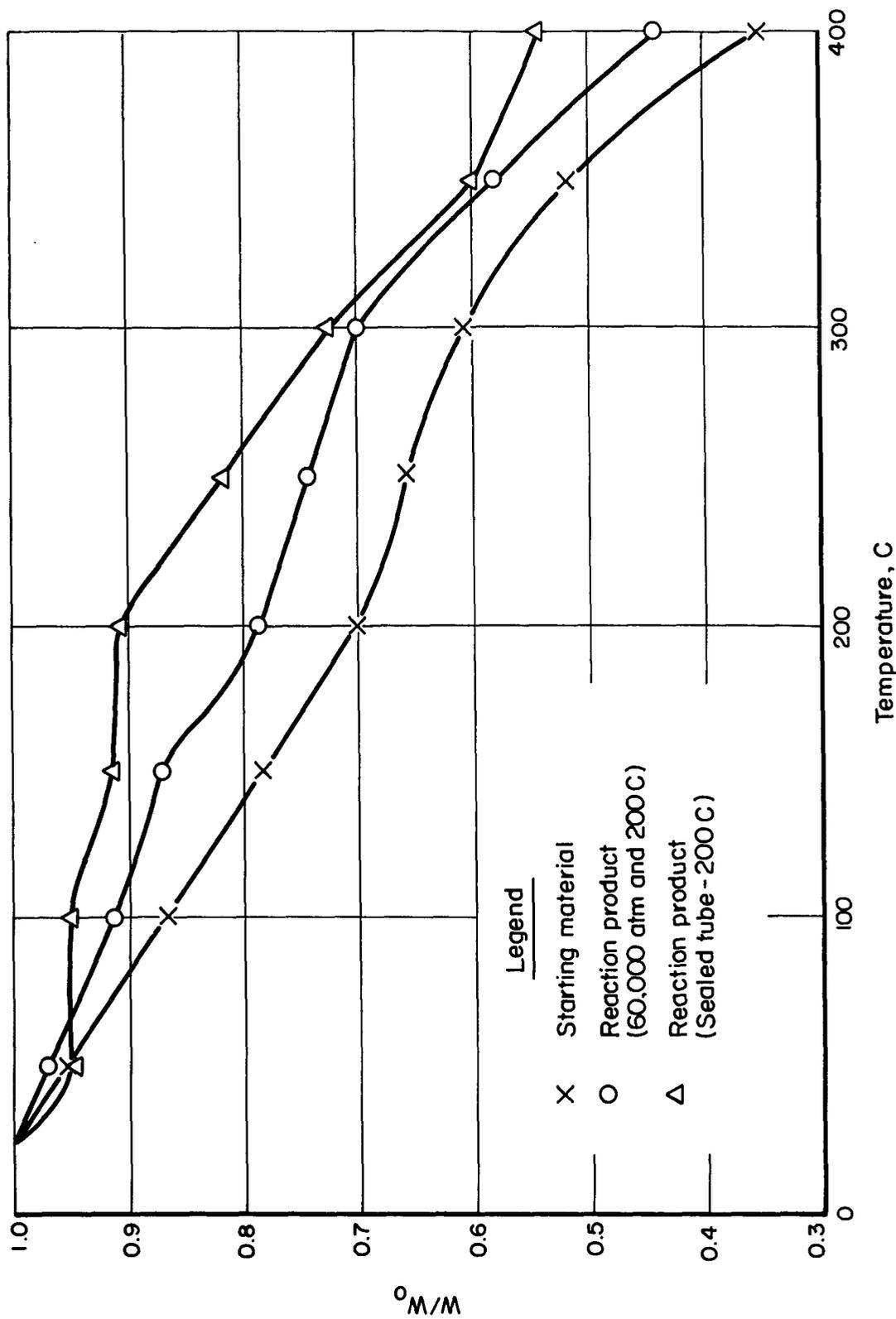


FIGURE 26. THERMOGRAVIMETRIC CURVES FOR THE DIPHENYLSILOXY-ALUMINUM-ISOPROPOXIDE POLYMER AND ITS PRESSURIZED AND UNPRESSURIZED REACTION PRODUCTS

product, and the unpressurized products. The slightly greater stability found for the unpressurized material reflects the inhibition of reaction which pressure appears to effect in this case.

Arsenosiloxanes

The arsenosiloxane reportedly having the composition $\text{As}[\text{OSi}(\text{C}_6\text{H}_5)_2\text{O}]_3\text{As}$ was unaffected by pressures up to 60,000 atmospheres at temperatures as high as 400 C for periods of several hours. However, when pressurization was conducted at 500 C for 3 hours definite structural changes occurred. As indicated by the infrared spectrum, these appeared to be breaking of the silicon-carbon bonds. Unpressurized samples held at 500 C for a 3-hour period did not degrade quite as extensively. This case was the only one encountered in this study in which high pressure appears to have increased the rate of decomposition of a material. This decomposition was not measurably affected by increasing the pressure to 75,000 atmospheres.

A linear polymer formulated as $\text{AsO}(\text{OH})_2[\text{OSi}(\text{C}_6\text{H}_5)_2\text{OAsO}(\text{OH})]_n\text{OH}$ underwent decomposition when subjected to 60,000 atmospheres at 100 C. However, increasing the pressure on this material to 75,000 atmospheres markedly inhibited the decomposition. Pyrolysis occurred readily when the material was pressurized at 200 C and 60,000 atmospheres.

These materials do not seem to offer any promise of forming new polymers or thermally stable products as a result of pressurization.

Phthalocyanines

Low polymers of copper phthalocyanine, containing 6 to 8 units of monomer, can be prepared by reacting pyromellitic dianhydride, urea, and copper (II) chloride at ordinary pressure. Several experiments were performed to investigate the possibility of obtaining higher polymers of this type by reaction under very high pressure.

Experiments with the mixture mentioned above have indicated that the product obtained under combined pressure and heat is a urethane rather than a phthalocyanine. At 75,000 atmospheres no reaction occurred below 200 C. At 250 C the reaction mixture darkened, became insoluble in ethanol, and its infrared spectrum indicated urethane formation. At 300 C the mixture pyrolyzed.

When the pressure was raised to 90,000 atmospheres these changes were much less extensive than 75,000 atmospheres. Consequently, the pressure was dropped to 60,000 at 250 C, and increased reactivity resulted. Urethane was still formed rather than phthalocyanine, however, similar reactions occurred at 45,000 and at 30,000 atmospheres at 250 C.

With the introduction of a catalytic amount of ammonium molybdate into the reaction mixture, pressurization at 30,000 atmospheres and 250 C resulted in a black mass which appeared to be pyrolyzed. By reducing the temperature to 200 C, at both 30,000

and 60,000 atmospheres the catalyzed mixture reacted to form a greenish product which appeared to be polymeric. This product was insoluble in common organic solvents and was thermally stable to 300 C.

Time has not permitted complete investigation of this system. The results of the most recent experiments indicate that phthalocyanine polymers of high molecular weight may possibly be formed in a catalyzed mixture by reaction at moderate pressure and a temperature in the vicinity of 200 C.

Aluminoxanes

Aluminum phenoxide was prepared by the reaction of aluminum with phenol. For this reaction, phenol (62.7 grams) was heated to reflux and a catalytic amount of iodine added. Aluminum turnings (6 grams) were added slowly, over a period of 5 hours, to keep the reaction under control. The excess phenol was distilled from the mixture at reduced pressure (1 mm Hg) and the product was then distilled at 340 C (1 mm Hg). The resulting aluminum phenoxide preparation was a yellowish-white solid which had a melting range of 205 to 220 C as prepared. After being redistilled the product melted at 240 to 242 C and was light yellow.

When pressurized, the aluminum phenoxide did not undergo significant change at 60,000 atmospheres and 250 C. After pressurizing at 75,000 atmospheres and 300 C, reduction in the amount of Al-O-C bonding, as shown by infrared spectrum, was indicative of aluminoxane polymer formation. However, the same result occurred when the compound was heated at 300 C in an evacuated tube without pressurization.

It appears that pressure does not have any effect on aluminum phenoxide that cannot be achieved simply by heating.

V. EXPERIMENTAL SECTION - INORGANIC MATERIALS

Ultrahigh Pressure - High-Temperature Apparatus

The ultrahigh pressure, high-temperature device used in most of this experimental program is a modified Hall belt apparatus⁽¹¹⁾ which was described in detail in ASD-TDR-62-73 dated January, 1962.⁽¹²⁾ The belt is an internally heated compressible gasket device. Subsequent modifications were made to improve the pressure-temperature capabilities of the belt apparatus. A set of more massive binding rings than those originally employed, equipped with a tungsten carbide die with the same angles and aperture (0.5 in.) but a smaller diameter (2 in. OD), was acquired for this purpose. The internal sample geometry and configuration were not changed (cf. Reference 12, Figure 23b). The modified apparatus with a 12-degree tungsten carbide die was calibrated by means of the electrical resistance discontinuities in bismuth at 25,000 atmospheres (bismuth I-II transition) and 87,000 atmospheres (bismuth V-VI transition) (Figure 27) as based on the revised absolute-pressure scale.^(13, 14) The efficiency of the

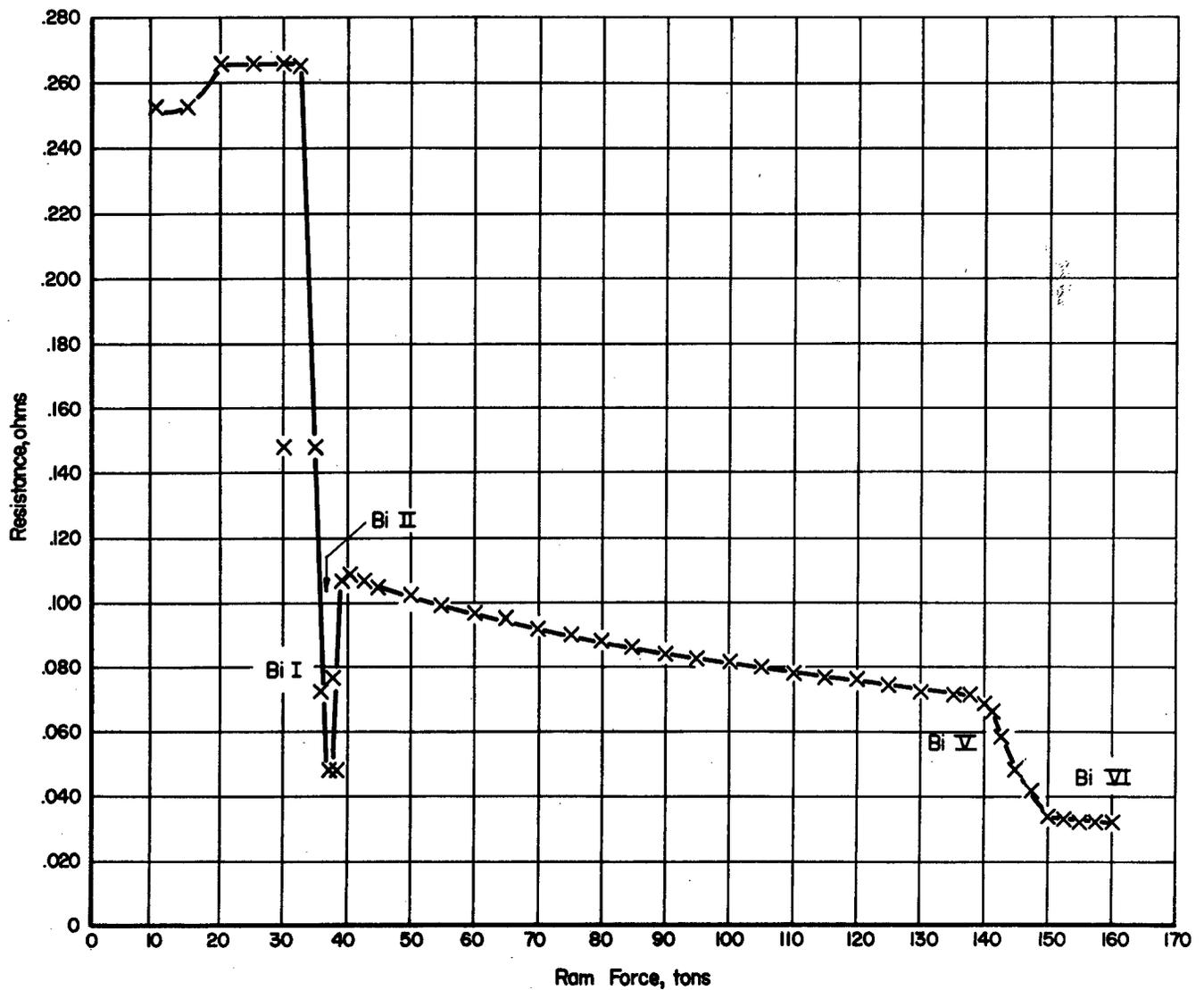


FIGURE 27. CALIBRATION OF THE MODIFIED BELT APPARATUS WITH A 12-DEGREE DIE BY MEANS OF THE Bi I-II AND Bi V-VI ELECTRICAL RESISTANCE TRANSITIONS

modified belt apparatus is essentially the same as the earlier version with the less massive binding rings. High-pressure high-temperature runs may be made routinely in the modified belt to 95,000 atmospheres and 1300 C for periods of days. Above 95,000 atmospheres the frequency of failure increases markedly, principally as a result of piston failure and subordinately as a result of die failure. Many of the pistons and dies appear to fail as a result of shock effects which are due to blowout of the gasket material. The maximum pressure achieved at high temperature in the modified belt was about 105,000 atmospheres based on linear extrapolation from the high bismuth transition at 87,000 atmospheres.

During the latter part of this program a Wilson girdle apparatus⁽¹⁵⁾ was obtained for experimental work. The girdle is an internally heated high-pressure device which consists of a steel die with a conical aperture and matching tungsten carbide pistons. When it is modified by addition of a compressible sandwich gasket of pyrophyllite sheathed with polyethylene, the device is capable of achieving up to 130,000 atmospheres at sustained high temperatures above 1000 C.⁽¹⁶⁾ Although the modified girdle is less efficient than the belt in the sense that it requires a greater ram force to obtain a given internal pressure, further modifications using a one-piece compressible pyrophyllite gasket with the same internal configuration show that the upper bismuth transition at 87,000 atmospheres is obtained at 150 tons. The girdle with these modifications and this internal geometry, therefore, is as efficient as the belt apparatus. Inasmuch as the girdle device with the one-piece gasket has been successfully subjected to loads of 250 tons several times without blowout whereas the belt device generally fails at loads greater than 180 tons (105,000 atmospheres), it may be possible, if the girdle device is linear above 87,000 atmospheres as it is at lower pressures, to achieve internal pressures on the sample as high as 145,000 atmospheres at sustained high temperature. The major difficulty with the girdle device at present is temperature measurement. To date it has not been possible to lead out thermocouples at high pressure, and temperatures must be estimated by wattage input to the heater tube. Further work on this problem is continuing in this laboratory.

Experimental Results

Effect of Pressure on Sulfides

Exploratory experimental work on the effect of high pressure and simultaneous high temperature on a group of sulfides, viz., Sb_2S_3 (stibnite), As_2S_3 (orpiment), Bi_2S_3 (bismuthinite), Ag_3SbS_3 (pyrargyrite), HgS (cinnabar), PbCuSbS_3 (bournonite), FeS (troilite), and Fe_{1-x}S (pyrrhotite), was carried out under the conditions given in Table 11. The high-pressure products were evaluated by X-ray powder-diffraction methods and incident-polarized-light microscopy. Because of the reactivity of Sb_2S_3 with respect to platinum above 500 C, it was run in gold heater tubes at the higher temperatures; the other sulfides were run in platinum heater tubes.

No changes were detected in any of the sulfides with the exception of FeS and Fe_{1-x}S . The former is paramagnetic stoichiometric FeS (troilite) from Del Norte County, California, and the latter is ferromagnetic nonstoichiometric iron-deficient Fe_{1-x}S (pyrrhotite) with $x = 0.13$ from Riondell, B. C. Stoichiometric troilite is

TABLE 11. EXPLORATORY HIGH-PRESSURE HIGH-TEMPERATURE
EXPERIMENTS ON SULFIDES

Sample	Pressure, atm	Temperature, C	Time, hr
Stibnite (Sb ₂ S ₃)	1	500	18
	48,000	610	18
	50,000	650	4
	60,000	490	25
	60,000	300	45
	70,000	200	42
	70,000	750	14-1/2
Orpiment (As ₂ S ₃)	50,000	310	16
	60,000	240	22-1/2
	80,000	300	16
Bismuthinite (Bi ₂ S ₃)	60,000	400	16
	60,000	200	16
Pyrargyrite (Ag ₃ SbS ₃)	60,000	350	14
	80,000	300	12
Cinnabar (HgS)	60,000	400	16
	70,000	500	61
	80,000	350	18
Bournonite (PbCuSbS ₃)	70,000	400	20
	70,000	250	15
Troilite (FeS)	60,000	600	44
	60,000	1150	20
	60,000	1000	20
	65,000	900	24
	65,000	500	1
	80,000	1050	14
Pyrrhotite (Fe _{1-x} S)	25,000	900	24
	26,000	680	80
	26,000	370	22
	50,000	700	20
	70,000	800	22
	70,000	360	22
	80,000	700	45
	80,000	1000	16
FeS ₂	80,000	700	2
	80,000	900	16

hexagonal, but highly nonstoichiometric pyrrhotite is monoclinic.⁽¹⁷⁻¹⁹⁾ When Riordell pyrrhotite ($\text{Fe}_{46.7}\text{S}_{53.3}$) is subjected to pressures between 50,000 and 70,000 atmospheres at temperatures below 900 C, the product contains about 3 to 5 per cent of a second phase which is readily detectable in polished section by incident-light microscopy. This new phase occurs as minute (<15 microns), discrete, apparently single-crystal grains disseminated through a relatively coarsely crystalline, granular aggregate of the original pyrrhotite. It is distributed as intergranular chainlike networks and as inclusions in the pyrrhotite. The phase was tentatively identified as pyrite (FeS_2) by optical methods. This is supported by the presence of a faint pattern for FeS_2 superimposed on the X-ray powder pattern of pyrrhotite and is confirmed quantitatively by a quantitative electron probe microanalysis of the new phase for iron. Once the identity of the phase was established as FeS_2 , it followed that the composition of the starting Fe_{1-x}S must have changed in the direction of greater stoichiometry as a result of the p-t conditions to which it was subjected. Further, FeS_2 inclusions were not detected in the pyrrhotite subjected to 80,000 atmospheres at 1000 C. It is possible to determine the composition of iron monosulfide between 50 and 46 atomic per cent iron by means of the recent determinative curve of Arnold and Reichen⁽²⁰⁾ which relates the magnitude of the (102) interplanar spacing to composition. On this basis, the pressurized pyrrhotite which contains FeS_2 inclusions shows a compositional change in the direction of increasing stoichiometry ($\text{Fe}_{46.7}\text{S}_{53.3} \longrightarrow \text{Fe}_{47.6}\text{S}_{52.4}$). When stoichiometric FeS is subjected to pressure it becomes slightly nonstoichiometric below 850 C (approaching 49 atomic per cent iron), but it becomes markedly nonstoichiometric above 850 C (approaching 47.6 atomic per cent iron). No microscopically detectable new phases accompany this compositional shift indicated by the determinative curve of Arnold and Reichen. As a working hypothesis it is proposed that this compositional shift involves the subsolidus exsolution of FeO from the troilite, and a few weak lines on the X-ray powder-diffraction patterns support this possibility. These experimental data strongly suggest that there is an equilibrium composition for iron monosulfide which is pressure and temperature dependent and that this composition can be approached from either stoichiometric or nonstoichiometric starting compositions.

The experimental data also indicate that the effect of pressure on the solvus curve between pyrrhotite solid solutions and the two-phase region (pyrite + pyrrhotite), determined by Arnold^(20,21) below 2000 atmospheres, is to shift the curve so as to increase the area of the two-phase region and decrease the area of the pyrrhotite solid solutions.

Effect of Pressure on Phosphates

Aluminum Phosphate

Anhydrous AlPO_4 is a structural analogue of quartz (SiSiO_4) and consists of a three-dimensional framework of aluminum and phosphorus coordination tetrahedra.⁽²²⁻²⁶⁾ It is a phosphate corresponding to the structural class of silicates known as the tectosilicates. AlPO_4 also has high-temperature forms corresponding to the tridymite and cristobalite forms of SiO_2 . Much work has been done on the synthesis and crystal growth of AlPO_4 because of its piezoelectric properties and its possible use as a substitute for quartz in electronic applications.⁽²⁷⁾

When Fisher reagent-grade AlPO_4 containing 24 per cent water, which corresponds to $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, is subjected to pressures greater than 23,000 atmospheres (cf. Table 12), the product is a coarsely crystalline (10μ to 300μ) single phase which has a unique X-ray powder-diffraction pattern (Table 13) and unique optical properties. The same new high-pressure phase may be produced by pressurizing the anhydrous quartz form of AlPO_4 (obtained by dehydrating the Fisher reagent) with distilled water (cf. Table 12). The high-pressure phase is stable through a broad pressure-temperature region ranging from 20,000 atmospheres and 600 C to at least 110,000 atmospheres and at least 1300 C (Figure 28). It is interesting to note that the melting point of anhydrous AlPO_4 decreased from greater than 1600 C at 1 atmosphere to about 950 C at 20,000 atmospheres in the presence of water; it is well known that there is a decrease of the same magnitude in the melting point of SiO_2 with increasing pressure in the presence of water.⁽²⁸⁾ The melting point of the high-pressure phase apparently increases with pressure to >1300 C at 80,000 atmospheres. The position of the liquidus line on the equilibrium diagram in the region of the minimum is controlled by two high-pressure symmetrically zoned products. Both of them had glass in the center of the heater tube, but one had the quartz form of AlPO_4 on either end, whereas the other had the high-pressure form on either end. This is a thermal-gradient effect at high pressure.

The high-pressure phase produced from either the Fisher hydrated reagent or the quartz form of AlPO_4 plus water was wet when the sample capsules were opened. A thermogravimetric analysis of a 20-mg sample of the high-pressure phase was made in vacuum using a Sartorius-Elektrona microbalance sensitive to 1 microgram. The results showed that this phase lost 5.95 per cent by weight between 500 and 850 C and did not lose weight below 500 C. Its infrared absorption spectrum shows the presence of structurally bound (OH). The liquid in contact with the high-pressure phase, therefore, represents the excess water in the initial reactants which is not incorporated in the structure of the solid. Samples of two high-pressure products (36,000 atmospheres and 1000 C, and 50,000 atmospheres and 900 C) were washed with distilled water. The pH of each leach liquor was strongly on the acid side and in each case a strong test for phosphorus was obtained with ammonium molybdate and benzidine, whereas only a weak reaction for aluminum was obtained with the very sensitive alizarin red S test. This suggests a pressure-induced change in the Al/P stoichiometry of the solid as follows:



A 90-mg coarsely crystalline single-phase sample of the high-pressure phase was prepared for quantitative chemical analysis by making three runs at 50,000 atmospheres and 900 C. This sample is free from extraneous phases as shown by microscopic examination and by X-ray powder diffraction. The high-pressure phase assays 47.4 per cent Al_2O_3 , 45.1 per cent P_2O_5 , and 6.0 per cent LOI for a total of 98.5 per cent. Two P_2O_5 determinations checked very closely and the LOI is equivalent to that obtained by thermogravimetric analysis of a sample prepared at 80,000 atmospheres and 900 C. The missing 1.5 per cent is almost certainly due to a small error in the alumina assay. The amount of structurally bound water in the high-pressure phase is evidently independent of the synthesis pressure in the range 50,000 to 80,000 atmospheres. By comparison, anhydrous AlPO_4 contains 41.8 per cent Al_2O_3 and 58.2 per cent P_2O_5 by weight. Thus, the qualitative indication of a change in the Al/P ratio of the solid has been confirmed quantitatively.

TABLE 12. EXPLORATORY HIGH-PRESSURE HIGH-TEMPERATURE EXPERIMENTS ON ALUMINUM PHOSPHATE

Starting Material	Pressure, atm	Temperature, C	Time, hr	Product
Hydrated reagent-grade AlPO_4	1	300	3	Quartz form of AlPO_4
	1	450	6	Ditto
	1	930	15	Cristobalite form of AlPO_4
	1	1200	16	Ditto
	15,000	650	20	Quartz form of AlPO_4
	18,000	600	16	Quartz form of AlPO_4 + trace of new phase
	20,000	1000	22	Glass + quartz form of AlPO_4
	23,000	1000	40	Glass + new phase
	23,000	600	20	New phase
	25,000	350	54	Complex, multiphase
	30,000	1000	48	Glass + new phase
	30,000	600	20	New phase
	36,000	1000	17	Ditto
	40,000	460	24	"
	60,000	640	24	"
	80,000	750	22	"
	80,000	900	31	"
	80,000	1000	41	"
	80,000	1300 [†]	31	"
90,000	1300	18	"	
110,000	1300 [†]	1	"	
Anhydrous quartz form of AlPO_4 + water	60,000	650	24	New phase
	50,000	750	24	"
Anhydrous quartz form of AlPO_4	60,000	1000	14	Quartz form of AlPO_4
	70,000	1150	24	Complex, multiphase
	80,000	750	18	Ditto
	80,000	1000	64	"
	80,000	1300	24	"
	90,000	1300	17	Complex, single phase
New phase	1	650	40	New phase + tr. quartz form + tr. cristobalite form
	1	750	16	Cristobalite form
	1	1200	15	Cristobalite form + minor quartz form

TABLE 13. X-RAY POWDER DIFFRACTION DATA FOR ALUMINUM PHOSPHATE PHASES

(FeK α_1 Radiation, $\lambda = 1.93597 \text{ \AA}$, Mn Filter, 57.3 mm Camera)

Fisher Reagent-Grade AlPO ₄ Containing 24 Per Cent of Water		Quartz Form of AlPO ₄ Obtained From Fisher Reagent-Grade AlPO ₄ at 400 C		Cristobalite Form of AlPO ₄ Obtained From Fisher Reagent-Grade AlPO ₄ at 1200 C		High-Pressure Form of Aluminum Phosphate							
d, A	I	d, A	I	d, A	I	d, A	I	d, A	I				
6.38	40	4.28	30	5.00	1	7.3	1	1.92	1	1.229	1	1.008	3
4.83	10	3.99	5	4.07	100	7.0	1	1.82	3	1.221	2	1.007	1
4.56	40	3.37	100	3.55	3	6.7	25	1.79	20	1.215	2	1.006	1
4.23	100	2.47	10	3.50	3	5.0	20	1.78	5	1.179	4	1.003	1
3.51	30	2.31	10	3.16	10	4.6	20	1.76	5	1.172	15	1.000	3
3.37	3	2.25	5	2.87	10	4.1	5	1.74	1	1.170	15	0.9940	7
3.08	5	2.14	7	2.50	20	3.9	2	1.72	3	1.168	4	0.9917	15
2.95	1	1.99	5	2.14	5	3.8	2	1.67	15	1.164	2	0.9885	4
2.70	75	1.83	15	2.04	3	3.63	10	1.65	3	1.159	4	0.9858	5
2.58	3	1.68	6	1.95	7	3.35	1	1.60	20	1.146	3	0.9842	15
2.485	15	1.55	12	1.89	5	3.32	2	1.59	15	1.135	1	0.9820	20
2.397	7	1.47	2	1.77	1	3.28	1	1.57	1	1.127	3	0.9810	3
2.284	7	1.392	15	1.75	2	3.20	100	1.56	15	1.125	3	0.9800	5
2.199	15	1.380	6	1.71	4	3.09	80	1.54	35	1.118	7	0.9773	20
2.153	3	1.303	5	1.65	1	3.06	3	1.53	20	1.113	7		
2.060	10	1.265	4	1.62	5	3.01	4	1.52	3	1.099	5		
1.950	15	1.235	2	1.58	3	2.92	2	1.50	1	1.090	5		
1.859	2	1.210	5	1.54	5	2.70	1	1.486	2	1.081	3		
1.757	3	1.196	5	1.507	4	2.66	2	1.456	3	1.074	3		
1.706	4	1.187	5	1.441	5	2.55	1	1.422	2	1.073	1		
1.662	10	1.161	4	1.410	2	2.51	45	1.393	10	1.062	5		
1.613	5	1.123	1	1.380	4	2.45	1	1.386	1	1.060	5		
1.578	4	1.090	10	1.362	2	2.41	1	1.352	1	1.058	5		
1.515	5	1.070	1	1.350	2	2.35	2	1.344	1	1.056	3		
1.484	7	1.051	5	1.312	4	2.32	5	1.325	5	1.052	5		
1.403	5	1.045	6	1.292	5	2.25	2	1.320	3	1.050	2		
1.347	7	1.024	6	1.245	1	2.20	10	1.310	3	1.045	1		
1.331	4	1.003	5	1.233	2	2.13	1	1.288	3	1.038	3		
1.291	5	0.9960	5	1.216	4	2.09	5	1.270	3	1.033	10		
1.278	4	0.9880	1	1.195	5	1.98	40	1.263	5	1.031	10		
		0.9823	3	1.185	5	1.96	35	1.255	30	1.023	3		
						1.95	35	1.247	2	1.014	2		
								1.239	2				

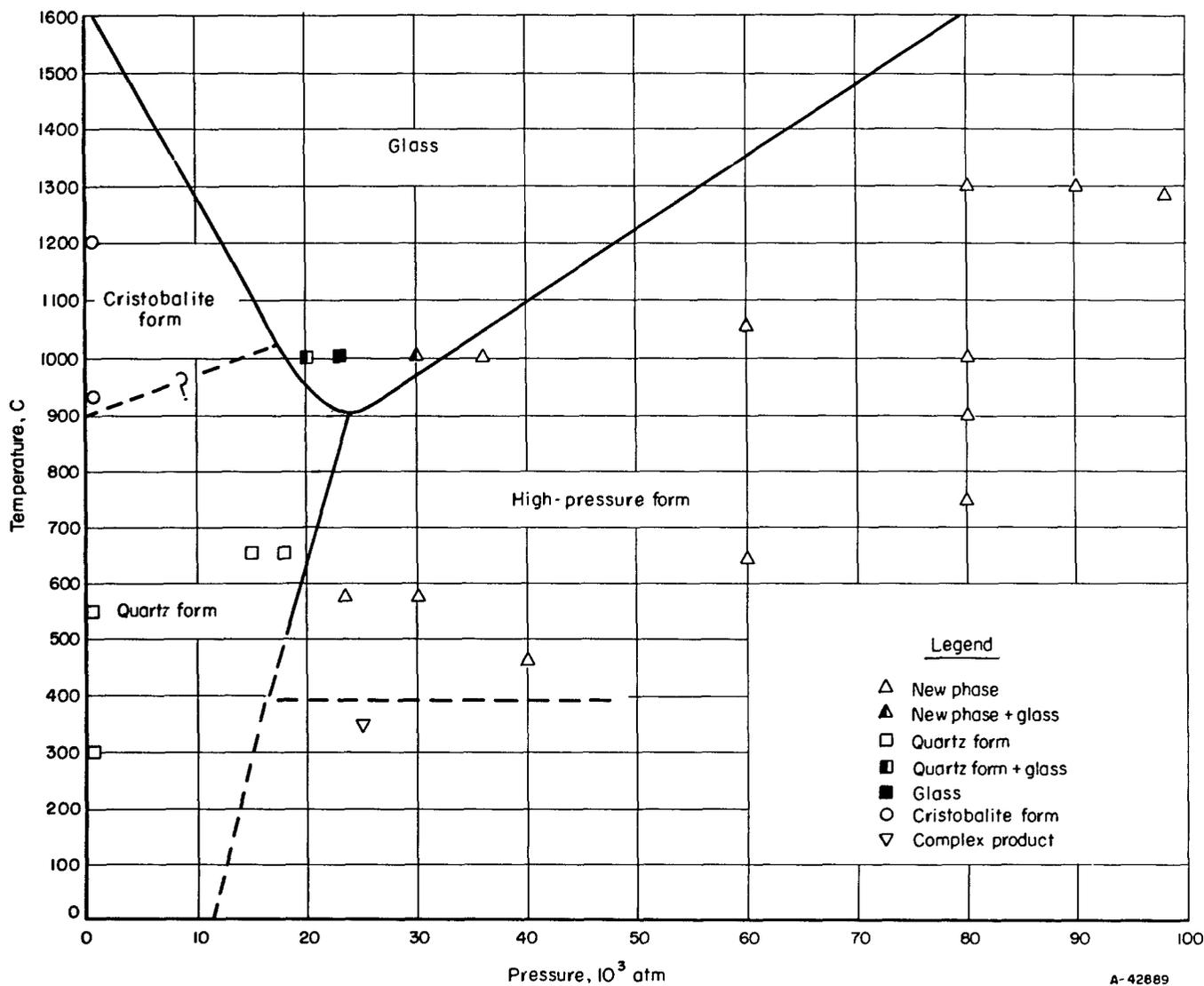


FIGURE 28. PHASE-EQUILIBRIUM DIAGRAM FOR THE SYSTEM $\text{AlPO}_4\text{-H}_2\text{O}$

The crystals of the high-pressure phase are colorless, range in size up to 300 microns, have dominantly bipyramidal morphology, and show both simple contact and multiple polysynthetic twinning with the composition plane parallel to a principal plane of the bipyramid. The X vibration direction is normal to the composition plane. The optical constants are: $\gamma = 1.635$, $\beta = 1.631$, $\alpha = 1.614$ (all ± 0.002), $\gamma - \alpha = 0.021$, $(-)$ $2V = 51$ degrees calculated from the refractive indices. The optical crystallography of this phase indicates that its symmetry is at least as low as orthorhombic, probably monoclinic, and possibly triclinic. This is in accord with X-ray power-diffraction data for this phase (Table 13) which constitute a very complex pattern. X-ray studies show that the new phase is not stable at ambient pressure and that it inverts on heating to the quartz and cristobalite forms of AlPO_4 (cf. Table 12).

The density of the new phase was determined empirically by float-sink methods using a centrifuge, methylene iodide - carbon tetrachloride mixtures, and acetylene tetrabromide. The experimentally measured density is $3.10 \pm .01$. The new phase is 18 per cent denser than the quartz form of AlPO_4 which has a density of 2.62.

Recent work on the effect of coordination on the principal infrared absorption band in reconstructively related pairs of polymorphs, such as GeO_2 (quartz) versus GeO_2 (rutile), SiO_2 (quartz) versus SiO_2 (rutile), AlAsO_4 (quartz) versus AlAsO_4 (rutile), has shown that a major change in cation coordination from 4 to 6 results in a 23 per cent shift in the main absorption band in the direction of increasing wavelength. (29, 30, 31, 32) Infrared absorption spectra of the hydrated aluminum phosphate starting reagent, the quartz form of AlPO_4 , and the high-pressure phase were obtained by means of the KBr window method using a Perkin-Elmer Infracord recording spectrophotometer (Figures 29, 30, and 31). They show that the principal absorption band is in essentially the same position (1050 to 1100 cm^{-1}) which is the characteristic group frequency of tetrahedrally coordinated $(\text{PO}_4)^{-3}$, $(\text{SiO}_4)^{-4}$, and $(\text{AlO}_4)^{-5}$ groups. The spectrum of the quartz form of AlPO_4 is very simple, in accord with the X-ray structural evidence that the cations are coordinated identically. The spectrum of the new phase, however, is relatively complex and shows additional very strong absorption bands at 980 and 1190 cm^{-1} . The band at 1190 cm^{-1} is typical of aluminum in octahedral coordination with oxygen (Figure 32). The infrared spectrum of the new phase, therefore, indicates that (1) there has been some change in cation coordination, (2) this change in cation coordination is not a major change for both cations as exemplified by a change from four- to sixfold coordination, and (3) phosphorus is still in fourfold coordination but aluminum may be in sixfold coordination.

The infrared absorption bands at 6.1, 3.2, and 2.95 microns in the starting material are probably due to weakly bound water of crystallization, in accord with the experimental results, whereas the absorption bands at 2.7 and 2.85 microns in the pressure-induced phase are indicative of structurally bound OH, in agreement with the results of thermogravimetric analysis. The quartz form of AlPO_4 is evidently anhydrous.

Studies of the quartz and rutile polymorphs of GeO_2 , SiO_2 , and AlAsO_4 (29,30,32,33) have shown that the effect of a change in cation coordination from four to six is to decrease the molar refraction by 12 ± 2 per cent. Polymorphs with the same cation coordination, i. e., quartz, tridymite, and cristobalite forms of SiO_2 , have differences in molar refraction relative to the quartz form of less than 3.5 per cent. The ambient-pressure forms all have positive differences; the high-pressure forms (BeF_2 coesite and SiO_2 coesite) have negative differences of about 1.8 per cent. Molar-refraction data for

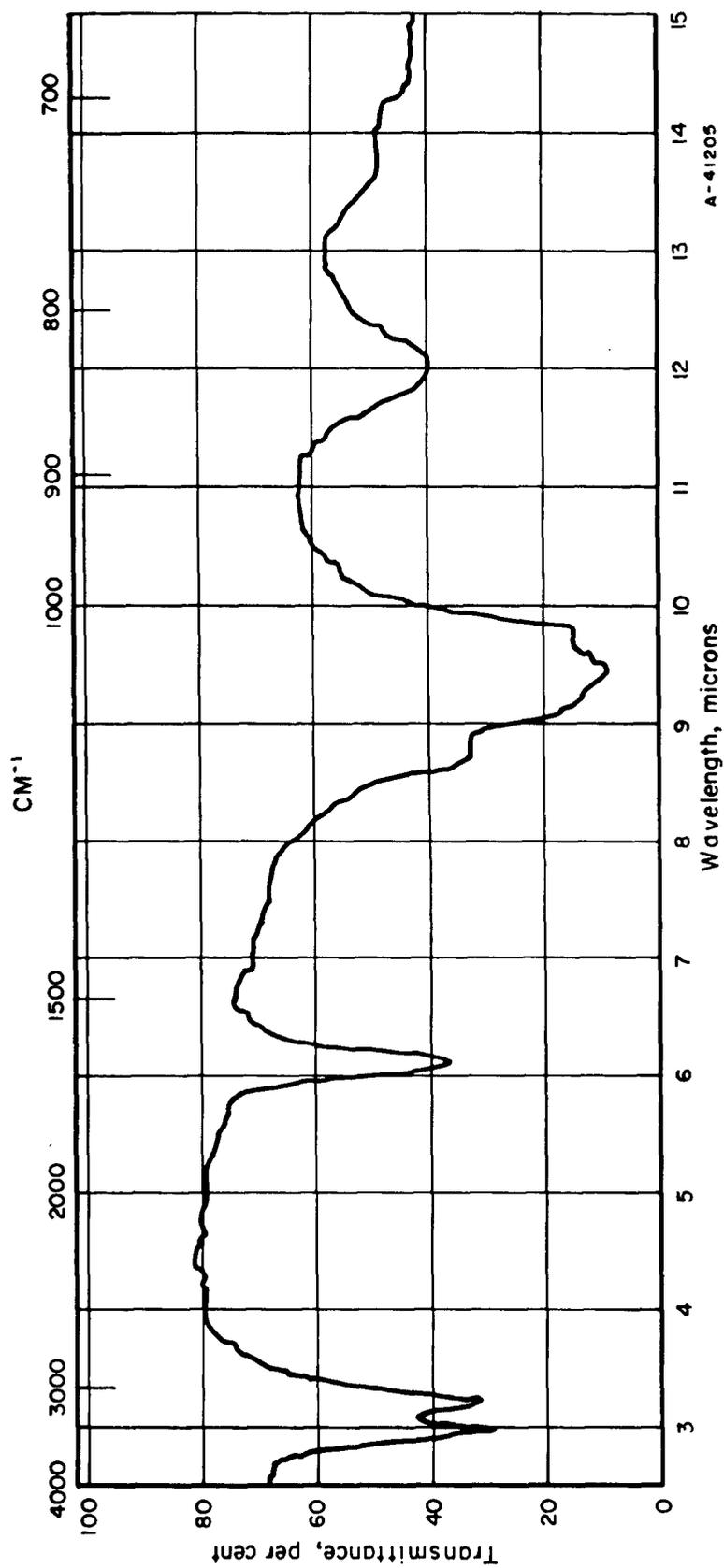
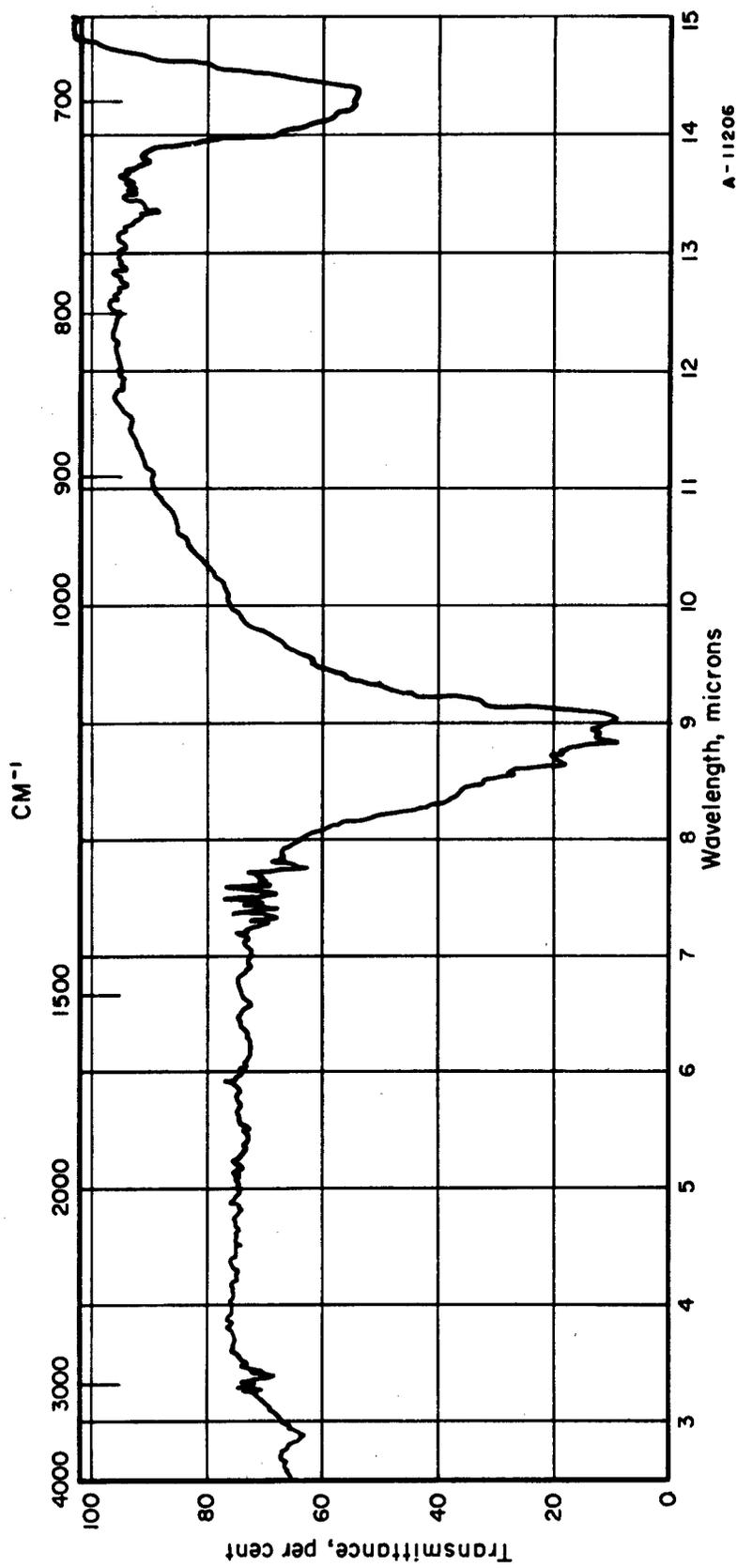
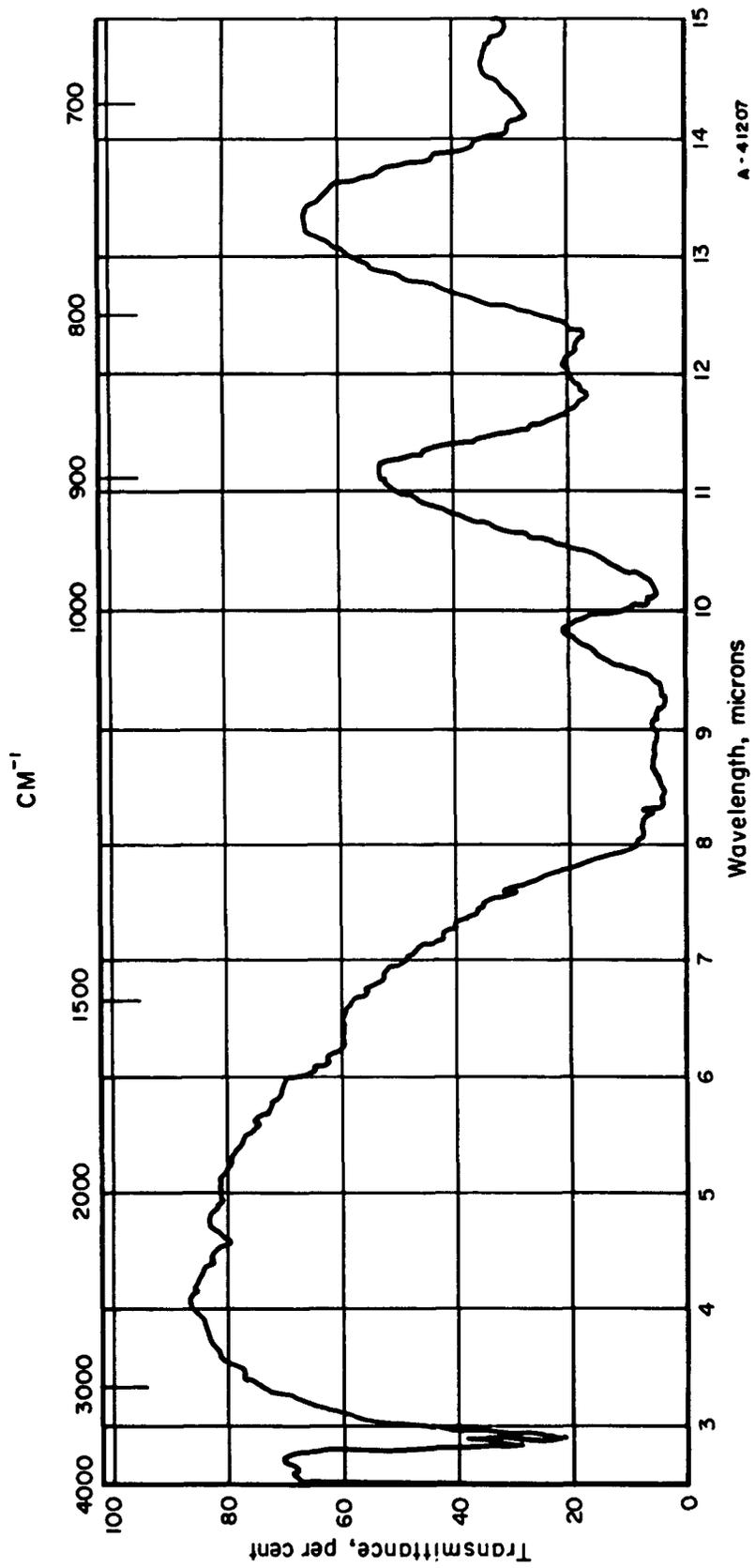


FIGURE 29. INFRARED SPECTRUM OF FISHER REAGENT-GRADE AlPO_4 CONTAINING 24 PER CENT OF WATER



A-11206

FIGURE 30. INFRARED SPECTRUM OF QUARTZ FORM OF $AlPO_4$ OBTAINED FROM FISHER REAGENT-GRADE $AlPO_4$ AT 400 C



A-41207

FIGURE 31. INFRARED SPECTRUM OF HIGH-PRESSURE FORM OF AlPO₄ OBTAINED AT 80,000 ATMOSPHERES AND 900 C

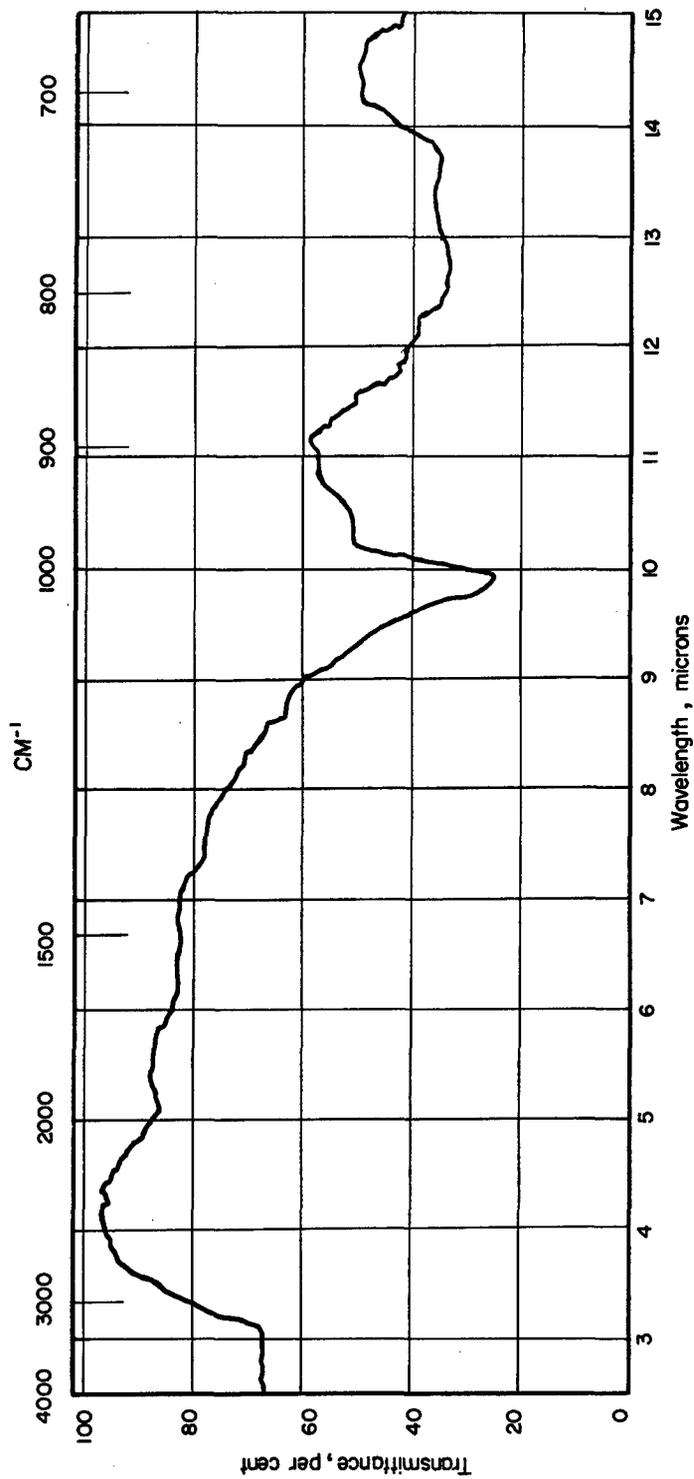


FIGURE 32. INFRARED SPECTRUM OF $\text{Al}(\text{OH})_3$ (GIBBSITE) IN WHICH ALUMINUM IS OCTAHEDRALLY COORDINATED WITH OXYGEN

AlPO₄ (quartz) and the new high-pressure phase are given in Table 14. These data suggest that the cation coordination in the high-pressure phase has not been completely changed with respect to the quartz form but that partial coordination changes may have occurred. The specific refractivity values (Table 14) show that both forms have essentially the same constant based on the Gladstone-Dale rule. The quartz form obeys the latter relationship fairly well as shown by $n_{\text{exp}} = 1.526$ and $n_{\text{calc}} = 1.501$, but the high-pressure form obeys it very well as shown by $n_{\text{exp}} = 1.627$ and $n_{\text{calc}} = 1.622$. On the basis of the stoichiometry of the high-pressure phase as shown by the chemical analysis and the additive character of the atomic refractions, it is possible to calculate the density of this phase by means of the molar-refraction relationship.^(34, 35) The calculated density of the high-pressure phase is 3.07, in good agreement with the experimentally determined value of 3.10.

TABLE 14. MOLAR REFRACTION AND SPECIFIC REFRACTIVITY OF AlPO₄ (QUARTZ) AND THE NEW HIGH-PRESSURE FORM OF ALUMINUM PHOSPHATE

Compound	Average Refractive Index	Density	Molar Refraction $\left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}\right)$	Specific Refractivity $\left(\frac{n - 1}{d}\right)$
AlPO ₄ (quartz form)	1.526 ^(a)	2.62	14.29	0.201
High-pressure form of aluminum phosphate	1.627 ^(b)	3.10	13.95	0.202
Per cent difference relative to the quartz form			-2.4	+0.5

(a) $(w^2 \epsilon)^{1/3}$.
 (b) $(\alpha \beta \gamma)^{1/3}$.

Samples of the high-pressure form of aluminum phosphate and of the quartz form of aluminum phosphate were mounted and polished for determination of their Knoop indentation hardness. The Knoop indentation hardness number of the quartz form based on 10 determinations with a 10-gram load ranged from 591 to 868 with an average of 732. The Knoop indentation hardness of the high-pressure form based on 10 determinations with a 10-gram load ranged from 1512 to 1788 with an average of 1588. The variation in hardness in each phase is due to orientation effects in anisotropic structures. As was anticipated, the high-pressure form is significantly harder than the ambient pressure analogue. The corresponding hardness on the Moh relative scratchability scale is about 8.5. The high-pressure hydroxyl-bearing aluminum phosphate is thus harder than spinel and topaz and is almost as hard as α -Al₂O₃ (corundum).

The new phase was considered initially to be a hydroxyl-substituted AlPO₄ in which (OH)₄ proxied for (PO₄) tetrahedra in the structure. The ideal structural formula was represented as [H_xAl(PO₄)_{1-x}(OH)_{4x}]. Silicate analogues of this composition are known, viz. [A(SiO₄)_{1-x}(OH)_{4x}], where A may be U⁴⁺, Th⁴⁺, or Zr⁴⁺, and x may be as high as 0.33.⁽³⁶⁾ In the case of the aluminum phosphate, it is necessary to assume the presence of hydrogen for valence compensation. All the hydroxyl-substituted silicates, however, constitute a continuous isostructural series with their respective anhydrous forms (where x = 0), whereas the high-pressure aluminum phosphate is structurally unrelated to AlPO₄ (quartz form). Finally, the chemical stoichiometry of the new phase shows that the

atomic O/P ratio is greater than 4:1 which precludes the possibility of it being a framework-, ring-, chain-, or sheet-structure phosphate. It apparently belongs to the orthophosphate group which corresponds to the nesosilicates (orthosilicates) and which is characterized by the presence of discrete $[XO_4]$ tetrahedra in the structure. The oxygen atoms at the vertices of the tetrahedra are not shared by other tetrahedra but are linked together through other cations which in general occupy positions of higher coordination than does the phosphorus. Not enough data are available on phosphates of known structure to draw any generalizations relating structure with physical properties, but for silicates, the nesosilicates are characterized by high refractive indices and high density. Tectosilicates (i. e., quartz) are characterized by low refractive indices and low density. One would expect, therefore, that the nesosilicate structure and, by analogy, the orthophosphate structure would be favored by high pressure.

The high-pressure aluminum phosphate appears to have the ideal structural formula $[Al_2(PO_4)_2 \cdot Al(OH)_3]$ as deduced from the chemical analysis and structural considerations. It may well be the aluminum analogue of the lazulite-scorzalite-barbosalite $[MgAl_2(PO_4)_2(OH)_2]$ - $[Fe^{+2} Al_2(PO_4)_2(OH)_2]$ - $[Fe^{+2} Fe^{+3}(PO_4)_2(OH)_2]$ atomic substitution series (37, 38). The X-ray powder-diffraction pattern of the high-pressure aluminum phosphate strongly suggests that it is related to this isomorphous series. Further, the X-ray powder-diffraction data and the optical properties of the high-pressure phase suggest that it is closely related, if not equivalent, to an unnamed mineral from Westana, Sweden (U.S. National Museum Sample No. R5611), described by Gheith⁽³⁹⁾. The latter was erroneously labeled berlinite, the mineral name for the quartz form of $AlPO_4$. It has not as yet been analyzed chemically but reportedly contains aluminum and probably contains iron as well, as indicated by its relatively high refractive indices.

The crystal structure of the lazulite-scorzalite-barbosalite series was recently determined by Lindberg and Christ.⁽⁴⁰⁾ The phosphorus atoms are tetrahedrally coordinated with oxygen and the other cations (Fe^{+2} , Fe^{+3} , Mg, and Al) are octahedrally coordinated with oxygen. This is compatible with the coordination scheme for the high-pressure aluminum phosphate phase as deduced from the infrared absorption and molar-refraction data. The experimentally demonstrated pressure dependence (Figure 28) of what appears to be the pure aluminum analogue of the lazulite series may be due to the very small ionic radius of aluminum (0.51 Å) as compared with the ionic radii of the cations in the ambient pressure compositional variants (Mg = 0.67 Å, Fe^{+2} = 0.74 Å, Fe^{+3} = 0.64 Å, Mn^{+2} = 0.80 Å). Although aluminum occurs in octahedral coordination with oxygen in many structures which are stable at ambient pressure, including the lazulite structure, it is apparently not possible to place aluminum in the octahedral sites normally occupied by magnesium in lazulite, ferrous iron in scorzalite, and ferrous iron in barbosalite without the application of high pressure. Analogous relationships between coordination and ionic radius exist for the SiO_2 and $AlAsO_4$ polymorphs^(32, 33) and for high-pressure $FeVO_4$ and $CrVO_4$ ⁽⁴¹⁾ in which pressure favors the crystallization of compositional variants in structures of higher coordination than are normally obtained at ambient pressure.

The effect of high pressure and temperature on the anhydrous quartz form of $AlPO_4$ was explored over a broad pressure-temperature range (cf. Table 12). Unlike the hydrated aluminum phosphate which transformed to a single phase over the same p-t range, the anhydrous $AlPO_4$ yielded several multiphase products and one single-phase product. All of the products give complex X-ray diffraction patterns which are unique in that they are not equivalent to either the high-pressure phase obtained from the

hydrated starting material or to any of the known thermally dependent polymorphs of AlPO_4 .

Iron Phosphate

After the synthesis of the high-pressure form of aluminum phosphate, an exploratory high-pressure high-temperature program was carried out on iron phosphate to determine whether an iron analogue of the high-pressure aluminum phosphate could be synthesized. Baker reagent-grade ferric phosphate containing 23.5 per cent water was used for the experimental work which is summarized in Table 15. This reagent appears to be amorphous to X-rays. When the hydrated ferric phosphate is heated at 750 C at ambient pressure it transforms to anhydrous FePO_4 which has the quartz structure.^(42,43) The hydrated reagent is transformed under pressure and temperature to a deep blue, almost black phase (Phase I) which is isostructural, as shown by X-ray powder diffraction (Table 16), with the high-pressure hydroxyl-bearing aluminum phosphate. By analogy with the high-pressure hydroxyl-bearing aluminum phosphate, Phase I has the formula $[\text{Fe}_2(\text{PO}_4)_2 \cdot \text{Fe}(\text{OH})_3]$. Phase I is almost opaque in the polarizing microscope but it is transparent in very thin edges of fine particles. It is biaxial and shows very intense pleochroism in deep blue-green, olive green, and olive brown and very strong dispersion of the bisectrices and optic axes. Refractive indices could not be determined accurately because of the strong absorption. When Phase I is heated at ambient pressure at 600 C for 65 hours it remains unchanged except for a trace amount of the quartz form of FePO_4 ; when heated at 1000 C for 4 hours, it inverts to the quartz form of FePO_4 plus another phase of unknown identity.

When the hydrated ferric phosphate reagent was subjected to 45,000 atmospheres and 750 C, a small amount of a unique white phase (Phase II) was observed on the ends of the platinum sample capsule where the temperature is lower than the measured temperature of 750 C in the central part of the capsule. Much larger amounts of the white phase developed near the ends of the capsule in the 55,000- and 70,000-atmosphere runs, and the product of a run at 105,000 atmospheres and 800 C consisted solely of Phase II. When Phase II is heated at 600 C for 65 hours it transforms to the quartz form of FePO_4 . As expected from the relative magnitudes of the pressures required for their synthesis, the thermal experiments at ambient pressure show that Phase II is less stable than Phase I at ambient pressure. X-ray powder-diffraction data for Phase II is given in Table 16. Phase II is colorless under the microscope, biaxial with an optic angle about 90 degrees, one plane of cleavage with extinction against the trace of the cleavage planes of 45 degrees, high birefringence, and mean index of refraction >1.80 .

Infrared absorption spectra of the hydrated ferric phosphate starting reagent, the quartz form of FePO_4 , Phase I, and Phase II were obtained by means of the KBr window method using a Perkin-Elmer Infracord recording spectrophotometer (Figures 33-36). Although Phase I is isostructural with the hydroxyl-bearing high-pressure aluminum phosphate as shown by X-ray diffraction, their infrared patterns are evidently not similar. This discrepancy is tentatively ascribed to the practically opaque character of the iron phosphate. Dacheille and Roy have published infrared absorption spectra of a group of compounds with the quartz structure.⁽²⁹⁾ Their spectrum for FePO_4 (quartz form) is different from their spectra for either the quartz form of AlPO_4 or GaPO_4 and indicates the presence of water by virtue of absorption bands at about 3 and 6 microns.

TABLE 15. EXPLORATORY HIGH-PRESSURE HIGH-TEMPERATURE EXPERIMENTS ON IRON PHOSPHATE

Starting Material	Pressure, atm	Temperature, C	Time, hr	Product
Baker reagent-grade FePO ₄ containing 23 per cent of water	1	300	4	Amorphous
	1	750	16	Quartz form of FePO ₄
	10,000	700	16	Two-phase mixture plus trace of Phase I
	15,000	600	20	1:1 two-phase mixture: Phase I
	45,000	750	19	10:1 Phase I:Phase II
	55,000	650	18	4:1 Phase I:Phase II
	70,000	750	24	2:1 Phase I:Phase II
	105,000	800	24	Phase II
Phase I (a)	1	600	65	Phase I plus trace of quartz form of FePO ₄
	1	1000	4	Quartz form of FePO ₄ plus trace of another unknown phase
Phase II (b)	1	600	65	Quartz form of FePO ₄ plus trace of Phase II

(a) Phase I is a blue-black almost opaque material.

(b) Phase II is a white transparent material.

TABLE 16. X-RAY POWDER-DIFFRACTION DATA FOR IRON PHOSPHATE PHASES

(FeK α_1 radiation, $\lambda = 1.93597\text{\AA}$, Mn filter, 57.3 mm camera)

Quartz Form of FePO ₄ Obtained From Baker Reagent- Grade FePO ₄ at 750 C				High-Pressure Form of Iron Phosphate (Phase I)				High-Pressure Form of Iron Phosphate (Phase II)			
d,A	I	d,A	I	d,A	I	d,A	I	d,A	I	d,A	I
6.7	3	1.63	1	6.35	15	1.260	1	6.19	15	1.444	5
6.0	3	1.58	30	5.38	10	1.226	7	4.98	40	1.427	2
5.3	3	1.51	5	4.85	30	1.212	7	4.32	90	1.414	15
4.4	40	1.42	50	3.68	7	1.165	10	3.62	3	1.390	3
4.1	2	1.41	10	3.34	100	1.158	10	3.11	100	1.369	7
3.46	100	1.34	10	3.20	50	1.140	7	3.00	30	1.349	15
3.28	2	1.29	7	2.72	25	1.130	2	2.89	5	1.321	1
3.05	3	1.24	5	2.418	5	1.099 ^B	3	2.58	50	1.307	3
2.95	2	1.23	5	2.290	30	1.087 ^B	1	2.52	20	1.287	2
2.72	3	1.21	7	2.054	40	1.070	2	2.477	20	1.262	5
2.57	15	1.18	2	1.868	5	1.056	3	2.432	20	1.244	7
2.51	15	1.15	1	1.839	10	1.027	5	2.204	1	1.217	10
2.36	30	1.11	10	1.717	1	1.024	5	2.147	10	1.194	1
2.29	10	1.09	10	1.668	20	1.011	7	2.069	30	1.180	1
2.18	30	1.07	15	1.658	20	1.006	1	2.025	15	1.160	3
2.03	1	1.045	7	1.604	60	0.9967	1	2.006	30	1.121	3
1.87	40	1.026	5	1.593	4	0.9887	1	1.948	5	1.112	5
1.72	20	1.016	15	1.454	8	0.9829	4	1.896	10	1.106	5
1.67	2	0.985 ^B	10	1.372	2	0.9803	10	1.824	1	1.076	10
				1.299	25			1.804	1	1.069	3
								1.782	1	1.063	3
								1.738	7	1.054	4
								1.709	10	1.048	5
								1.667	2	1.042	5
								1.653	30	1.027	7
								1.610	5	1.011	3
								1.579	10	1.006	3
								1.569	10	1.004	5
								1.552	15	1.002	3
								1.527	1	0.9981	3
								1.511	1	0.9913	1
								1.475	5	0.9835	10
								1.465	5		

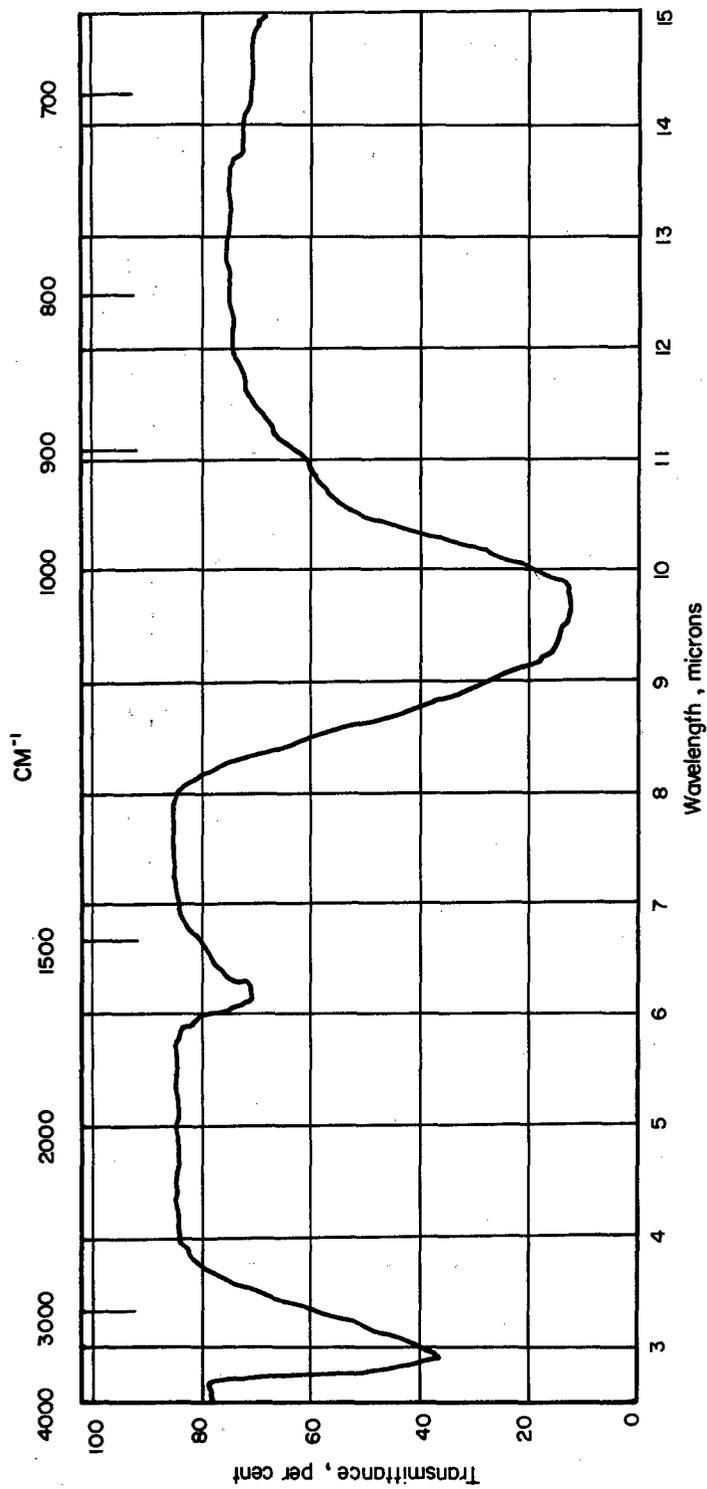


FIGURE 33. INFRARED SPECTRUM OF BAKER REAGENT-GRADE FePO₄ CONTAINING 23 PER CENT OF WATER

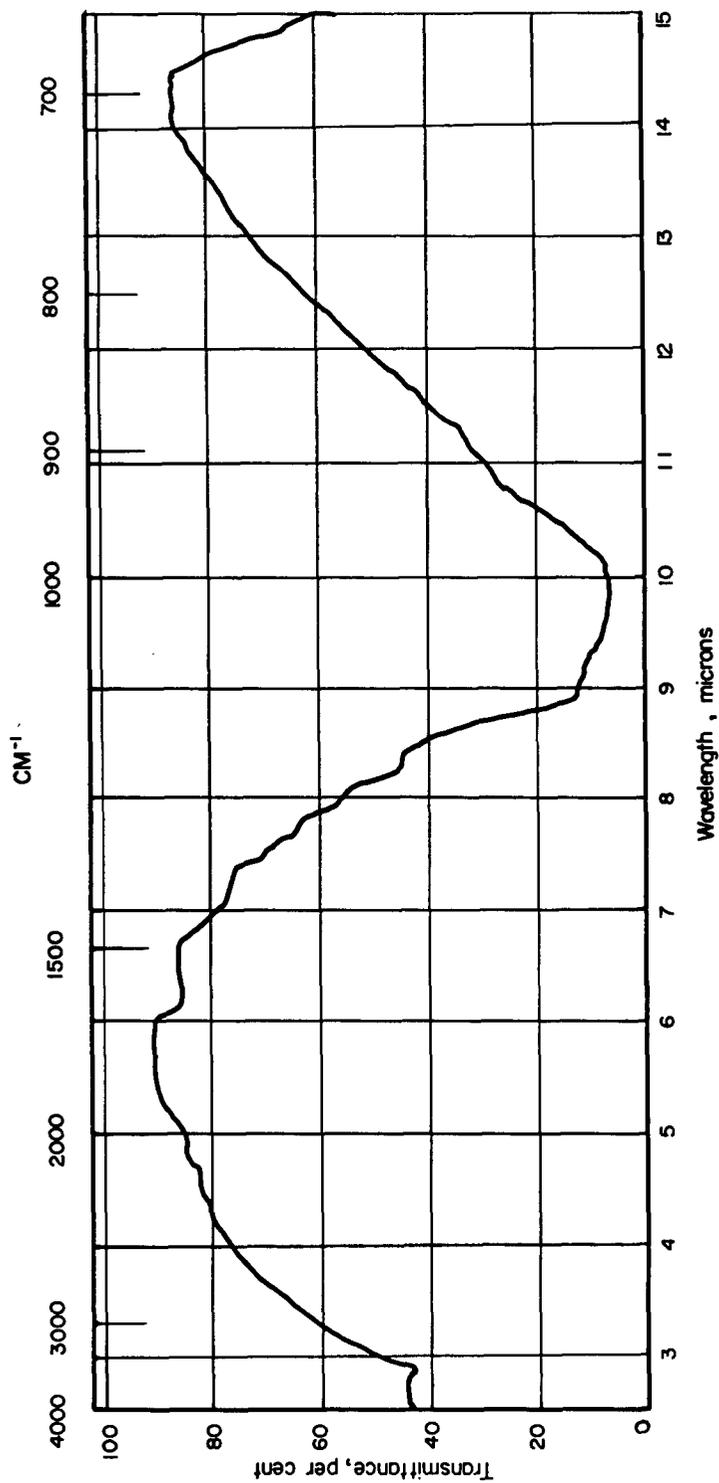


FIGURE 34. INFRARED SPECTRUM OF QUARTZ FORM OF FePO_4 OBTAINED FROM BAKER REAGENT -GRADE FePO_4 AT 750 C

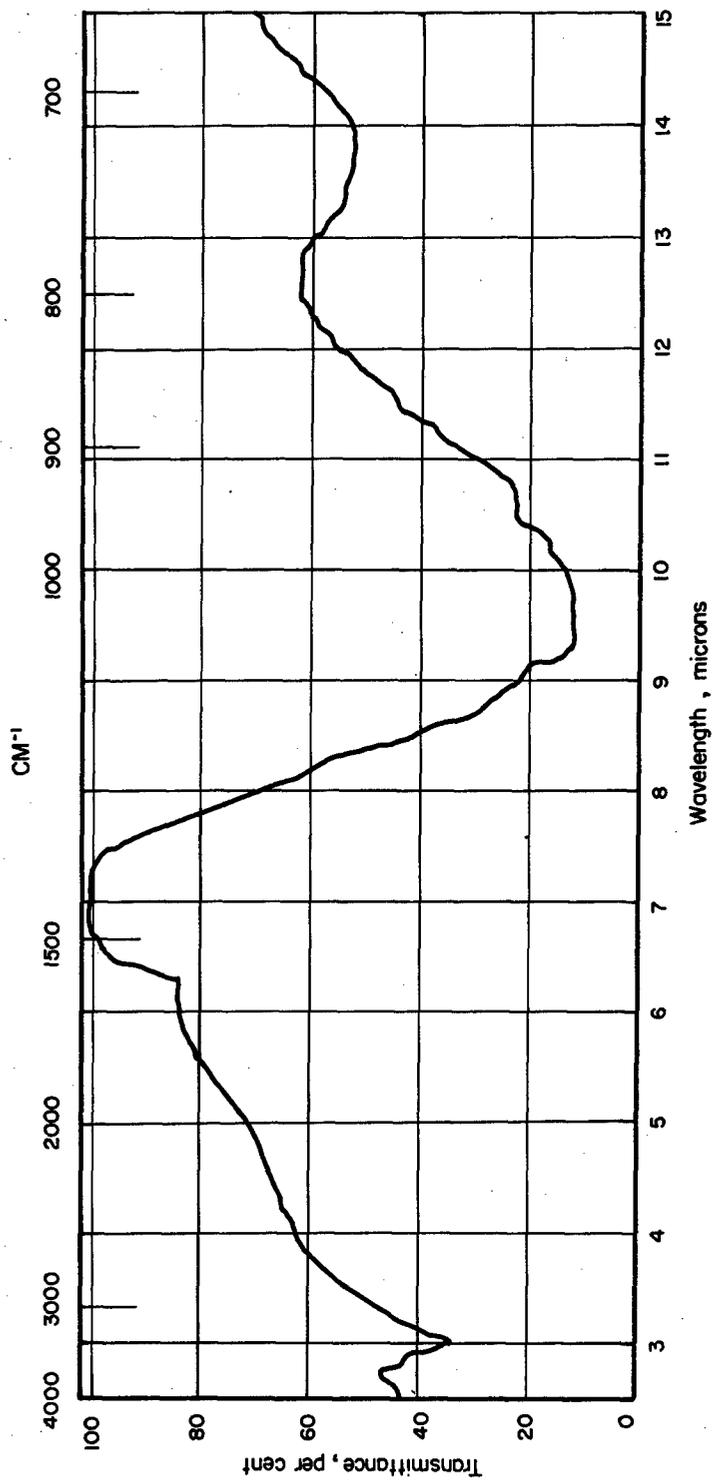


FIGURE 35. INFRARED SPECTRUM OF HIGH-PRESSURE FORM OF IRON PHOSPHATE (PHASE I) OBTAINED AT 45,000 ATMOSPHERES AND 750 C

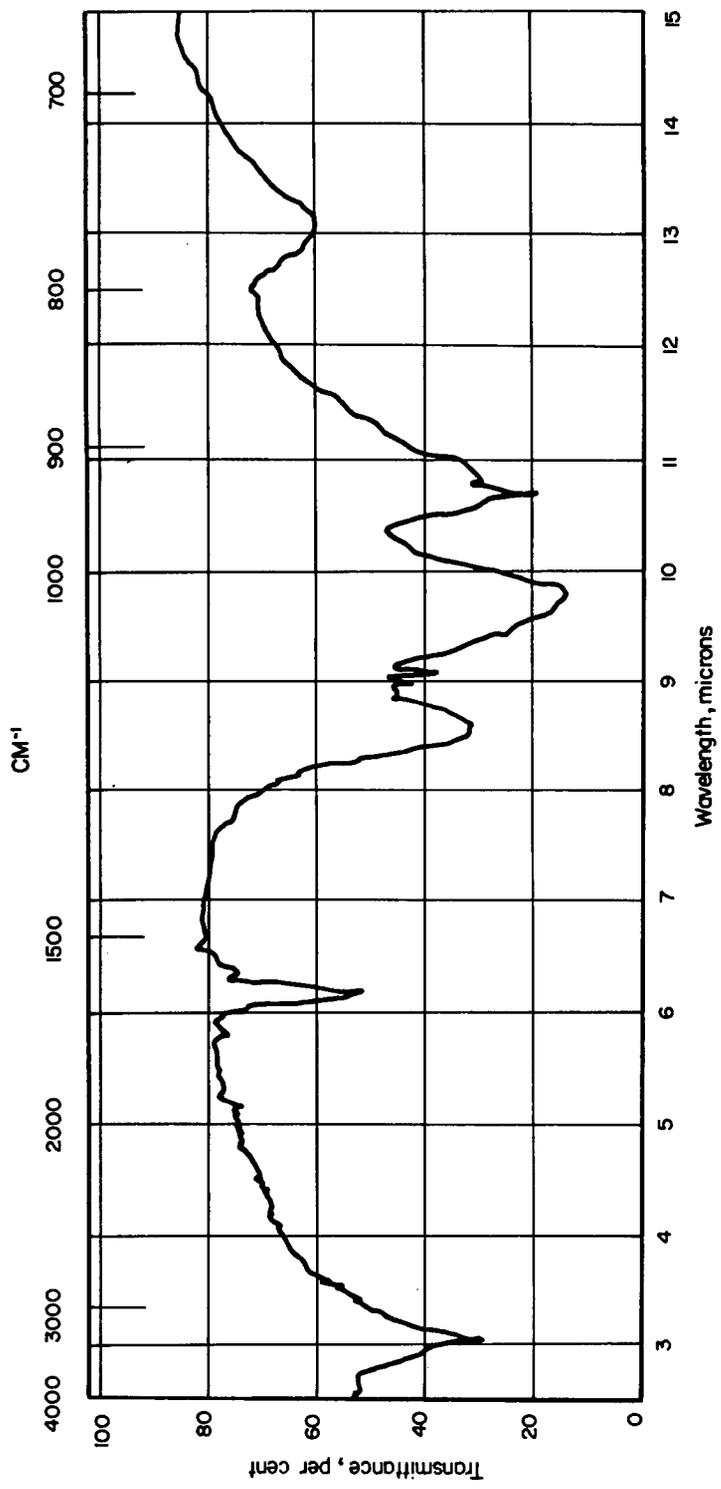


FIGURE 36. INFRARED SPECTRUM OF HIGH-PRESSURE FORM OF IRON PHOSPHATE (PHASE II) OBTAINED AT 55,000 ATMOSPHERES AND 650 C

This spectrum closely resembles the infrared spectrum of Battelle's Phase II (Figure 36). Inasmuch as Dacheille and Roy were doing high-pressure work on silica-structure phases including FePO_4 ⁽⁴³⁾, it is possible that they mistook Phase II for the quartz form. Correspondingly, Battelle's spectrum of the quartz form of FePO_4 (Figure 34) is in agreement with the spectra of the quartz forms of AlPO_4 and GaPO_4 published by Dacheille and Roy⁽²⁹⁾ and with Battelle's infrared spectrum of the quartz form of AlPO_4 (Figure 30).

Zirconium Pyrophosphate

Zirconium pyrophosphate was selected for high-pressure high-temperature experimentation because its crystal structure is well established⁽⁴⁴⁾, it is a representative compound of the pyrophosphate group, it is one compositional variant of a large isomorphous series ($\text{X}^{+4}\text{P}_2\text{O}_7$ where X may be zirconium, silicon, titanium, hafnium, or uranium), it is cubic which permits structural changes to be evaluated readily, and because zirconium is monovalent. The experimental conditions employed in this study are summarized in Table 17. Reagent-grade ZrP_2O_7 containing about 12 per cent water was obtained from Bios Laboratories, Inc. for this study. All pressure experiments were carried out on anhydrous cubic ZrP_2O_7 prepared by preheating the Bios material in air to 700 C.

TABLE 17. EXPLORATORY HIGH-PRESSURE HIGH-TEMPERATURE EXPERIMENTS ON ZIRCONIUM PYROPHOSPHATE

Starting Material	Pressure, atm	Temperature, C	Time, hr	Product
Bios reagent-grade ZrP_2O_7	1	700	4	Cubic form of ZrP_2O_7
Bios reagent-grade ZrP_2O_7 heated to 700 C	25,000	1000	18	Cubic form of ZrP_2O_7
	55,000	750	20	High-pressure form of ZrP_2O_7
	100,000	1000	3	Ditto
High-pressure form of ZrP_2O_7	1	600	65	"
	1	1000	3	Cubic form of ZrP_2O_7

A new high-pressure polymorph of zirconium pyrophosphate was prepared at 55,000 atmospheres and 750 C and 100,000 atmospheres and 1000 C. X-ray powder-diffraction data for the cubic polymorph and the high-pressure polymorph are given in Table 18. The new phase is white in powdered form and colorless under the microscope. It is uniaxial positive with $\epsilon = 1.773 \pm .003$, $\omega = 1.755 \pm .003$, and $\epsilon - \omega = 0.018$. The crystals have an average size of about 20 microns, but a few crystals as large as 40 microns were observed. None of the crystals show external morphology so that there is no direct indication whether this phase is tetragonal or hexagonal. The density of the

TABLE 18. X-RAY POWDER-DIFFRACTION DATA FOR
ZIRCONIUM PYROPHOSPHATE

($\text{FeK}\alpha_1$ radiation, $\lambda = 1.93597 \text{ \AA}$, Mn filter,
57.3 mm camera)

Cubic Form of ZrP_2O_7				New High-Pressure Form of ZrP_2O_7			
d, A	I	d, A	I	d, A	I	d, A	I
4.7	20	1.503	1	4.76	10	1.302	2
4.1	100	1.455	15	3.72	50	1.281	5
3.66	20	1.436	1	3.465	2	1.272	1
3.36	20	1.393	15	3.316	15	1.253	15
2.91	20	1.374	15	3.207	2	1.227	25
2.485	40	1.335	5	3.155	60	1.214	10
2.385	5	1.303	5	2.948	40	1.167	4
2.285	5	1.257	10	2.597	3	1.156	20
2.065	3	1.242	7	2.445	3	1.135	2
1.990	2	1.225	1	2.411	4	1.115	20
1.943	3	1.165	1	2.319	6	1.099	2
1.893	15	1.153	5	2.160	3	1.087	20
1.845	25	1.143	15	2.041	100	1.074 _B	2
1.795	2	1.130	1	1.873	10	1.061	30
1.745	1	1.120 _B	1	1.806	1	1.055	1
1.684	20	1.100	20	1.748	30	1.054	1
1.586	30	1.073	25	1.632	1	1.052	10
1.530	1			1.615	50	1.034	5
				1.586	5	1.029	20
				1.521	1	1.022	70
				1.485	5	1.005	1
				1.462	50	0.9954	2
				1.449	1	0.9928	7
				1.420	30	0.9862	30
				1.392	1	0.9817	3
				1.382	15	0.9796	2
				1.353	1	0.9730	10
				1.328	3		

Note: $a_0 = 8.26 \text{ \AA}$ in agreement with Reference (35).

new phase is $3.62 \pm .02$ as determined by float-sink methods using Clerici's solution (equal parts of thallos formate-thallos malonate in water). The high-pressure phase, therefore, is 15.7 per cent denser than the cubic form of ZrP_2O_7 which has a calculated density of 3.13 as based on its lattice parameter of 8.258 Å. ⁽⁴⁵⁾

The high-pressure phase does not change when heated in air at 600 C at ambient pressure for 65 hours. When it is heated in air at 1000 C at ambient pressure for 3 hours, however, it does invert to the cubic form. This indicates that the high-pressure phase is a polymorph of ZrP_2O_7 which is metastable at ambient pressure.

As discussed in greater detail in the section on aluminum phosphate, studies of polymorphic pairs related by reconstructive transformation have shown that the effect of an increase in cation coordination from 4 to 6 is to decrease the molar refraction by 12 ± 2 per cent. ^(29, 32, 33) Polymorphs with the same cation coordination have essentially the same molar-refraction values. Molar-refraction data for the cubic form and the high-pressure form of ZrP_2O_7 are given in Table 19. It is evident that the molar-refraction values are the same for the two polymorphs. On this basis it is concluded that there is no difference in the primary cation coordination of these polymorphs and that the increase in density is due to closer packing of the coordination polyhedra. As indicated by the structure of the cubic form, zirconium is in octahedral coordination and phosphorus is in tetrahedral coordination in these polymorphs. ⁽⁴⁶⁾ The specific refractivity values in Table 19 show that this pair of polymorphic forms obeys the Gladstone-Dale rule very well.

TABLE 19. MOLAR REFRACTION AND SPECIFIC REFRACTIVITY OF THE CUBIC FORM OF ZrP_2O_7 AND THE NEW HIGH-PRESSURE POLYMORPH OF ZrP_2O_7

Form of ZrP_2O_7	Average Refractive Index	Density	Molar Refraction $\left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \right)$	Specific Refractivity $\left(\frac{n - 1}{d} \right)$	Sources of Data
Cubic	1.657	3.13	31.16	0.210	Reference (35) and this report
High pressure	1.761 ^(a)	3.62	30.17	0.210	This report

(a) $(\omega^2 \epsilon)^{1/3}$.

Infrared absorption spectra of the cubic form and the high-pressure form of ZrP_2O_7 were obtained by means of the KBr window method using a Perkin-Elmer Infracord recording spectrophotometer. The spectra are shown in Figures 37 and 38. The spectrum of the cubic form is in agreement with that given by Steger and Leukroth⁽⁴⁷⁾. It is evident that there is a change in the general transmission characteristics of the two forms, with the high-pressure form transmitting broadly through the 8 to 13-micron range. The main absorption bands are essentially the same, although they are displaced about 0.2 microns toward the higher wavelengths in the high-pressure form. Recent studies of the effect of coordination on the main absorption bands in reconstructively related polymorphs has shown that a change in cation coordination from 4 to 6 results in a 23 per cent shift in the main absorption band in the direction of increasing wavelength. ⁽²⁹⁻³²⁾ Conversely, the absence of any significant shift in the main absorption band is indicative of the same coordination in a pair of

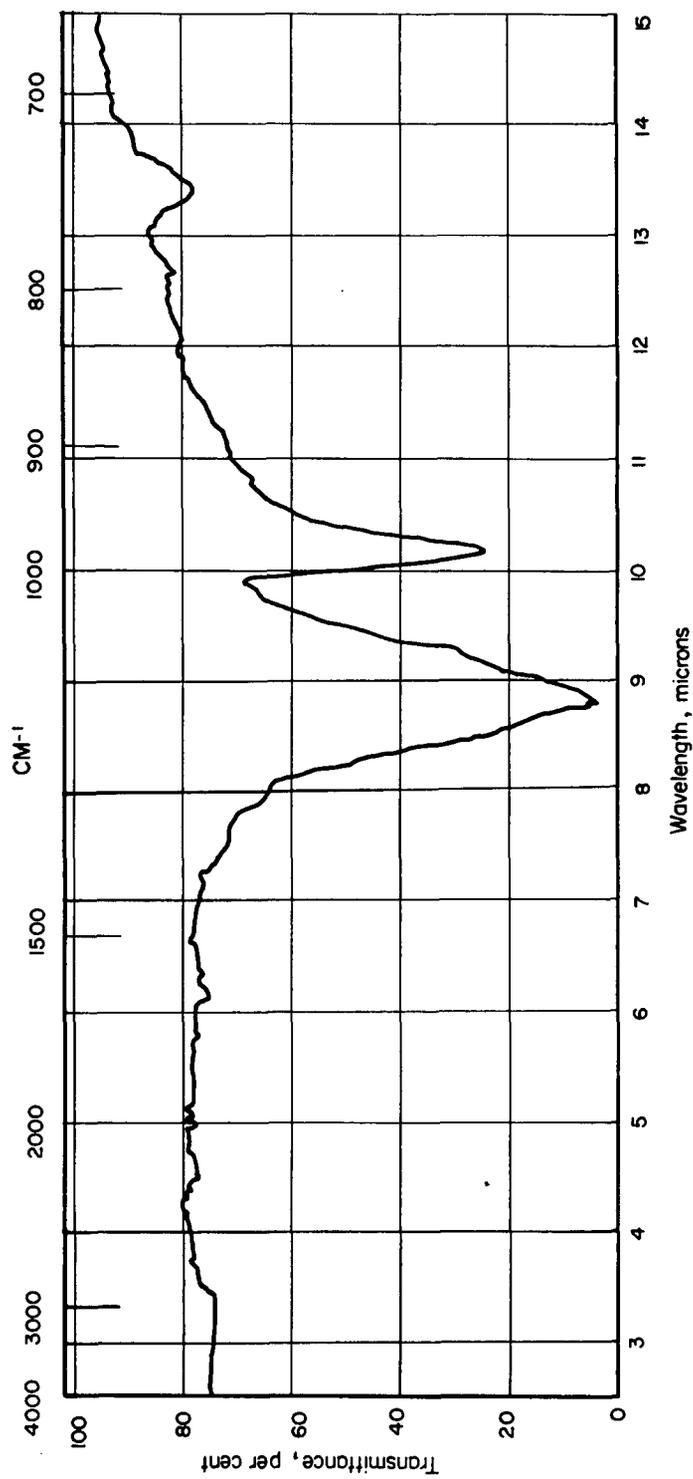


FIGURE 37. INFRARED SPECTRUM OF CUBIC FORM OF ZIRCONIUM PYROPHOSPHATE OBTAINED FROM BIOS REAGENT-GRADE ZrP_2O_7 AT 700 C

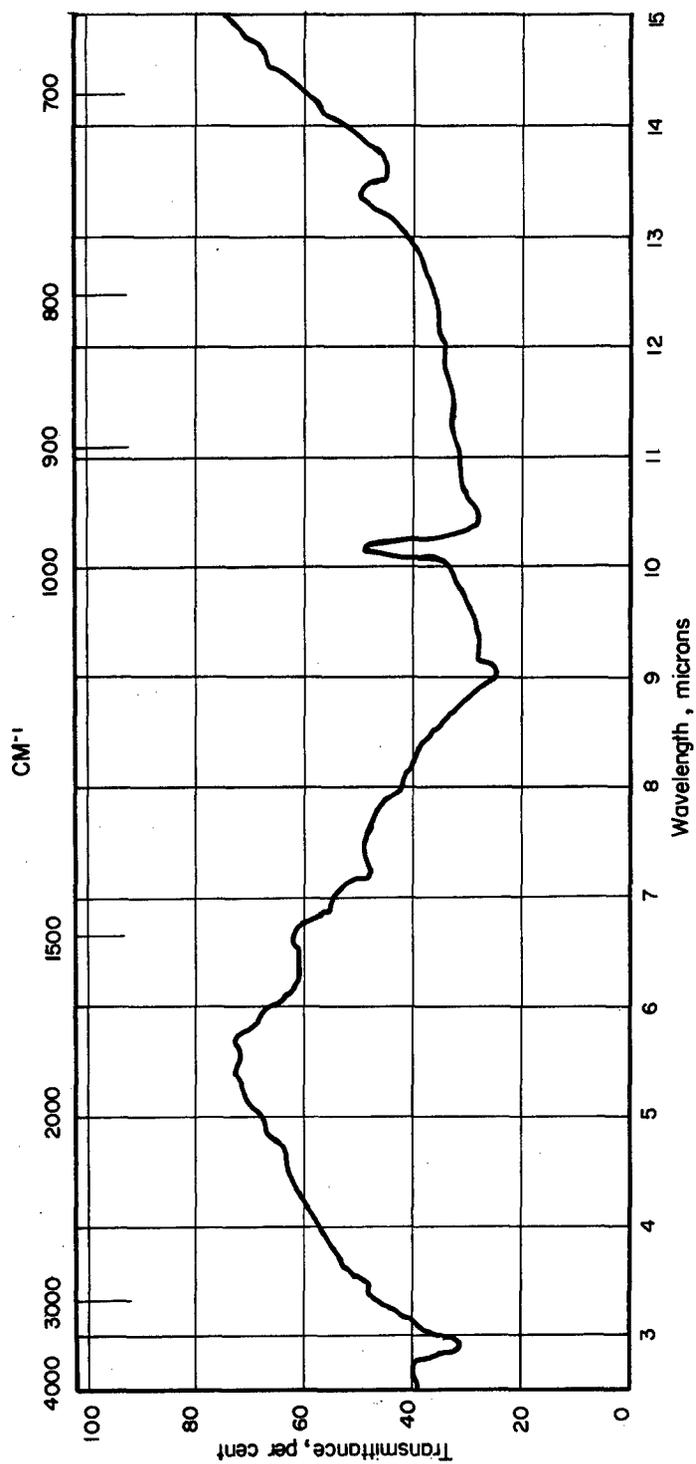


FIGURE 38. INFRARED SPECTRUM OF HIGH-PRESSURE FORM OF ZrP_2O_7 OBTAINED AT 55,000 ATMOSPHERES AND 750 C

polymorphs. Figures 37 and 38 show that the basic coordination scheme of the cubic and the high-pressure forms is the same, in agreement with the deductions from the molar-refraction data.

Other Phosphates

High-pressure high-temperature experiments were carried out on BPO_4 , and $[\text{Ca}_5(\text{PO}_4)_3\text{OH}] \cdot \text{BPO}_4$ was converted to the quartz modification⁽⁴⁷⁾ at 80,000 atmospheres and 750 C and at 90,000 atmospheres and 400 C. $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$ with the apatite structure remained unchanged at 90,000 atmospheres and 1000 C.

VI. CONCLUSIONS AND RECOMMENDATIONS

Organic Polymers

As a result of the experimental program just concluded on the effect of superpressure treatment on the properties and structure of organic polymers, polymerization of monomers, and nonmonomers, the following conclusions and recommendations are made.

- (1) The extreme compression conditions employed appeared to promote crosslinking and graft reactions in some monomer-polymer systems.
- (2) Chemical reactivity can be induced in normally nonreactive, non-monomer materials by superpressure treatment.
- (3) The superpressures used in the polymerization studies appeared to retard the reactivity of the system.
- (4) The effect of superpressure treatment on polymeric materials is in general small and varies with the polymer and compression conditions.
- (5) It is recommended that superpressure polymerization studies cover a sufficient range of pressures to provide positive correlation with results established at lower compressions.
- (6) It is recommended that temperature be incorporated as a parameter to raise the monomer solidification temperature.
- (7) It is recommended that polymerizations be studied with permanent radicals under suitable conditions of temperature and pressure such that the monomer is still in a liquid phase.
- (8) It is recommended that further study be made of the reactivity of quinone under superpressures and elevated temperatures to establish the reaction mechanism to determine whether this or a similar reaction could be used to produce organic materials having unique and desirable physical or electrical characteristics.

Semiorganic Polymers

As a result of this investigation, the following conclusions were made: (1) addition reactions at double and triple bonds appear to be promoted by pressure, (2) such combinations as carbon-nitrogen, phosphorus-nitrogen, phosphorus-oxygen, carbon-sulfur, and phosphorus-sulfur should undergo reaction under pressure.

Further study of systems having multiple bonds is recommended.

Investigation of phthalocyanine-forming reaction mixtures at intermediate pressure also is recommended, because this approach seems to offer promise of forming higher polymers than can be obtained by heating.

Inorganic Polymers

The oxygen chemistry of pentavalent phosphorus is based on PO_4 tetrahedra which, like SiO_4 tetrahedra, may be linked together in various ways to form P_2O_7 ions, ring and chain ions of composition $(\text{PO}_3)_n$, layered structures, and infinite three-dimensional complexes. As a result, the phosphates and analogous vanadates and arsenates represent a wide range of structures and compositional variants on which to study the effects of ultrahigh pressure and high temperature. The synthesis of new high-pressure orthophosphates of aluminum and iron and of a new high-pressure pyrophosphate of zirconium as reported above is suggestive of the potential of the phosphate structures with respect to the study of pressure-dependent phase transformations and the properties of the resultant high-pressure phases.

It is suggested that a systematic study be undertaken on the effects of pressure and temperature on representative phosphates, vanadates, and arsenates of different structural types.

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