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EXPERIMENTAL INVESTIGATIONS RELATING TO THE PROPERTIES AND FORMATION OF COSMIC GRAINS

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I. INTRODUCTION

The interpretation of observations or theoretical analyses of interstellar processes requires a sound knowledge of relevant data. In many instances this can only be obtained by experiments carried out under appropriate conditions. This report is a general survey of the availability of such data applicable to the subjects of this workshop and the techniques for obtaining it. Laboratory investigations of extraterrestrial matter are discussed in the reports by Walker, Kerridge, and Wood.

There exist many significant measurements taken for other purposes but useful for astrophysical problems. It is necessary to use caution and good judgement when treating an astrophysical problem with data obtained for terrestrial purposes. Astrophysical conditions, particularly, temperature, pressure, and surface to volume ratio often differ greatly from those under which the measurements were made. The user needs to be alert to the reliability of the data for the conditions under which it is being used. This constraint often applies when experiments have an astrophysical objective because the experiment may not be possible under actual conditions, for example, at the low densities of interstellar or circumstellar clouds. The next section lists the major collections of experimental data, many of which are well known. Some are more specialized or more recent and not well known.

This report is not intended as a comprehensive review of experimental results or techniques. Its purpose is to serve as a guide to sources of data and call attention to laboratory procedures which have or will supply new, much needed results. New measurements are continuously being carried out and the researcher needs to follow up the literature for such data.

II. SOURCES OF EXPERIMENTAL DATA

1. General

There are a number of comprehensive collections of data covering physics, chemistry, geophysics and other scientific disciplines. These are listed below.

1. Landoldt-Bornstein-Tables of Numerical Values and Functions (in German)
2. International Critical Tables
3. Handbuch der Physik
4. Handbook of Physics and Chemistry - Chem. Rubber Co.
5. Handbook of Geochemistry

There are in addition to these compendia many smaller or more specialized tables of numerical data which are available in libraries. A continuing source of new or improved data is the "Journal of Physical and Chemical Reference Data" available through the American Chemical Society. As with all the above publications, some small fraction of the material is relevant to cosmic dust.

In addition, the series of Annual Reviews e.g. Physical Chemistry, Nuclear Physics, Material Science, will have pertinent articles. Also, to be kept in mind are a growing collection of review publications, e.g. Reviews of Modern Physics, Advances in Physics, Reports on Progress in Physics, Contemporary Physics, Chemical Reviews, Accounts of Chemical Research, Soviet Physicks Uspekhi (Soviet Reviews of Modern Physics), Progress in Surface Science and others. Finally, there are the numerous journals of current research in physics, chemistry and related subjects.

2. Spectroscopy

The standard reference on spectroscopy is Herzberg's very comprehensive four volume treatise "Molecular Structure and Molecular Spectra". Other sources which supplement that are, Pearse and Gaydon (1965), Suchard (1975, 1976), and Rosen (1970). Ultraviolet spectra of organic molecules are displayed in two multivolume sets, Lang (1961) and U. V. Atlas of Organic Compounds, Plenum Press, N.Y. Clar (1964) presents the near ultraviolet-visible spectra of polynuclear aromatics.

There are a number of collections of infrared spectra of molecules and minerals. For molecules, perhaps the best is the Coblenz Society "Evaluated Infrared Reference Spectra" available from Sadtler Research Laboratories. Inorganic species are treated in "Infrared Spectra of Inorganic Compounds (3800-45 cm^{-1}) R. A. Nyquist and R. O. Kagel and "The Sadtler Infrared Spectra Handbook of Minerals and Clays" edited by J. R. Ferraro. Many texts and reference books on spectroscopy and photochemistry will show spectra and yield other references and as always, journal articles and reviews need to be examined. Fluorescent spectra of a variety of organic molecules and numerous references prior to 1966 may be found in "Fluorescence and Phosphorescence Analysis" edited by D. M. Hercules.

3. Optical Properties of Solids

a. Minerals

The most detailed analyses of interstellar grains have been devoted to the interpretation of interstellar extinction and scattering. This is still an active field of research. The prime requirement is knowledge of the index of refraction of appropriate solids. Some of this data may be found in the works cited in Section 1. Much more extensive data appears in publications concerned with optics of solids. Chapter 10 in "Absorption and Scattering of Light by Small Particles" by C. F. Bohren and D. R. Huffman contains references to several sources. This book is an excellent reference for the entire subject of the interaction of light with small particles. An earlier work by Huffman (1977) emphasizes interstellar grain problems.

In recent years the interest in cosmic grains has resulted in studies of astrophysically interesting solids including measurement of refractive indices. Measurements of the wavelength dependence of the index of refraction, 0.185-2.6 microns, for 24 rocks and minerals are listed and displayed in Chapter V, "Optical Properties of Inhomogeneous Materials", W. G. Egan and T. W. Hilgeman, Academic Press, N.Y., 1979. Optical properties of small metallic colloids, including small size effects, were treated by Hughes and Jain (1979). A number of materials considered as possible grain components have been measured by several investigators. A representative, and not comprehensive list is given in Table 1. Extensive references are given in the above two reports and in the papers cited in Table I.

An important measurement for the study of grains at high temperatures in circumstellar shells or stellar atmospheres is the temperature dependence of the optical properties. Essentially all existing data on optical constants or absorption spectra refer to room temperature. The absorption of a quartz layer heated to temperatures in the range 600-1600 K was measured by Dvurechenskii et al. (1978).

Table I

Measured Optical Properties of Proposed Grain Constituents

Material	Spectral Range	Property	Reference
1. Silicates (lunar rocks)	10-1600 cm^{-1}	Dielectric constants	Perry et al. Moon, 4, 315, 1972
2. MgO (0.1 micron cubes)	400-800 cm^{-1}	Emissivity	JOSA 71, 393, 1981 O. Matamura, M. Cho
3. MgO	IR	Reflectivity, 8K-1960K	J. R. Jaspers et al., Phys. Rev. 146, 526, 1966
4. Silicates	4-14 microns	Emission and absorption spectra	J. R. Stephens, R. W. Russell, Ap. J. 228, 780, 1979
5. Silicates phyllosilicates	7-50 microns	Absorption spectra	A. Zaikowski, et al. "Solid State Ap." ed. (p 151) Wickramasinghe, Morgan, Reidel, 1976

6.	Silicates	1026-1640 A	Complex index of refraction	P. L. Lamy, Icarus 34, 68, 1978
7.	Hydrated silicates, carbonaceous chondrites, amorphous carbonates	2.5-30 microns	Absorption spectra	R. F. Knacke, W. Kratschmer, Astron. Astroph., 92, 281, 1980
8.	Silicates	7-14 microns	Emission spectra	Ap. Sp. Sci. 1979 65, 47
9.	Hydrous Silicates	7-140 microns	Extinction coefficient 2K-1400K	C. Koike, H. Haseqawa, T. Hattori, Ap. Sp. Sci. 88, 89, 1982
10.	Terrestrial Silicates	0.2-50 microns	Complex index of refraction	J. B. Pollack, O. B. Toon, B. Khare, Icarus, 19, 372, 1973
11.	Amorphous Quartz Grains r=200 A	1400-400 cm^{-1}	Complex index of refraction	T. R. Steyer, K. L. Day, D. R. Huffman, Appl. Optics, 13, 1589, 1974
12.	Terrestrial and Vapor Condensed Silicates	4-14 micron	Absorption and emission spectra	Stephens and Russell (1979)
13.	Silicate Minerals	infrared	Absorption	F. M. Penman (1975)
	Non-silicate Minerals	infrared	Absorption	F. M. Penman (1976)
14.	Quartz	2.5-5.5 micron	Emission spectrum 600K-1600K	Dvurechenskii et al. (1978)
15.	Silicates	2-20 or 8-14 microns	Emission spectra	Rose (1977)

b. Carbon

A number of measurements of the optical constants of graphite from the ultraviolet to the infrared for light incident both perpendicular and parallel to the basal plane have been carried out. References to these papers and discussions of the results are given by Huffman (1977) and Draine and Lee (1984). Corresponding data for glassy carbon have been presented by Williams and Arakawa (1972) and for amorphous carbon by Duley (1984). There is an apparent discrepancy between Duley's results and the measured extinction by amorphous grains. The calculated extinction by small amorphous particles do not show any broad ultraviolet extinction bumps whereas measured extinction curves by Stephens (1980) for 0.03-0.01 micron particles have a distinct peak between 4 and 4.25 micron^{-1}. Similar results were obtained at Goddard where the peak shifted to shorter wavelengths as the size was reduced.

Amorphous carbon films have also been prepared by a glow discharge technique. Anderson (1977) reports a study of the structure, electrical and optical properties of films condensed from a glow discharge in C_2H_2. Lin and Feldman (1983) with a generally similar procedure observed the C-H stretch at 3.4 microns and the CH_2 bending mode at 6.9 microns. The vibrational spectra of hydrogenated, amorphous Si-C films was investigated by Wieder et al. (1979). The effect of possible hydrogen contamination on some of the properties in Anderson's films may be significant. Similar experiments were carried out by Watanabe et al. (1982). The hydrogen concentration is very dependent on deposition temperature.

There have been several experimental studies of extinction by small carbon grains and silicon carbide grains. These are listed in Table II. A later attempt by Hecht and Donn to extend the measurements reported in item 3 was not successful. The very small size grains could not be obtained. However, a regular structure in the extinction curve, generally similar to that reported for the smaller size distribution in the early experiments, regularly appeared. It is believed that the structure is an artifact of the experimental arrangement and thus raises serious questions about the reality of the 1978 data. Further work is needed on the extinction of small graphite grains and the transition from graphite to large polynuclear aromatics.

Table II

Extinction by Carbon and Silicon Carbide Grains

Grain Structure	Experiment	Reference
1. Graphite	Polarization by aligned grains	Cayrel and Schatzmon (1954)
2. Amorphous Carbon	Size and shape of condensate from vapor	Lefevre (1967)
3. Graphite	Normalized extinction coeff., 350-650 nm, r<0.2 micron	Donn et al. (1968)
4. Amorphous Carbon	Extinction	Lefevre (1970)
5. Carbon Smoke	30 nm particles, probably mostly amorphous 120-600 nm	Day and Huffman, Nature, Phy. Sci. 243, 54, 1973
6. Amorphous Carbon	Size, structure, formation of vapor condensed particles	Kappler et al. J. App. Phy. 50, 308, 1979
7. Amorphous Carbon	Extinction 210 nm - 340 microns	Koike et al., Ap. Sp. Sci., 67, 495, 1980
8. Amorphous Carbon, SiC, Silicate Smokes	Extinction 130-800 nm, vapor condensed smokes	Stephens (1980)
9. Amorphous Carbon	Extinction 200 nm-40 micron	Borghesi et al., A&A, 142, 225, 1985
10. SiC	Mass abs. coeff., size distribution <1.5 micron	Dorschner et al. (1977) Astron. Nach., 298, 279
11. SiC	Mass abs. coeff., size distribution <4 micron	Friedemann, et al. (1981), Ast. Sp. Sci., 79, 405
12. Fe_3C	Mass abs. coeff.	Nuth et al. (1984) Ap. J., 290, L41

c. Laboratory Synthesized Non-Volatile Material

With a few exceptions, Table I deals with either terrestrial, lunar or meteoritic material. The exceptions are condensates from laser or arc vaporized material in items 4 and 15 respectively.

Measurements of the optical properties of laboratory synthesized material including small grains have also been carried out. Day (1974, 1976) prepared amorphous magnesium silicates by precipitation from solution and measured their infrared spectrum. Later, he produced amorphous films of magnesium and iron silicates (Day, 1979, 1981) by sputtering a mixed MgSi, Mg_2Si, FeSi or Fe_2Si target in an argon-oxygen atmosphere. The complex refractive indices were determined by dispersion analysis of the transmission measurements.

Amorphous silicate grains have also been obtained by condensation from a mixed vapor. In addition to condensing SiO and Mg+SiO to yield amorphous grains (Day and Donn, 1978a, b; Nuth and Donn, 1982, 1983) these experimenters also investigated changes in spectra and structure when grains were annealed for various time-temperature combinations (Nuth and Donn, 1983a, 1984). More recently experiments have been started at Goddard on the hydration of amorphous grains (Nuth et al., 1985).

Kratschmer and Huffman (1979) irradiated olivine with energetic protons to obtain a crystal with a high density of defects which would thus simulate an amorphous silicate. The infrared spectrum was similar to that of condensed amorphous silicates with structureless 9.7 and 18 micron interstellar features.

The possible role of carbon grains as sources of interstellar extinction started with the proposals by Loretta (1934) and O'Keefe (1939) that the irregular obscuration of RCr B stars was caused by condensation of a cloud of carbon. Caryel and Schatzman (1954) later suggested interstellar polarization could result from aligned graphite grains and measured the polarization of magnetically aligned grains. In 1962, Hoyle and Wickramasinge, carried the investigation further with the analysis of graphite formation in red giant stars.

These proposals were soon followed by the discovery of the 217.5 nm ultraviolet extinction feature Stecher (1965) and its interpretation in terms of graphite grains by Stecher and Donn (1965).

A variation of the graphite model was introduced with the proposal (Donn, 1968) that an array of polycyclic hydrocarbon molecules (Donn and Krishna Swamy, 1969) could act as Platt particles (Platt, 1956) and may account for the extinction. A preliminary account of experiments on the vapor phase absorption spectra as well as the thermal and photodissociation of polycyclic aromatic hydrocarbons was given by Stief et al. (1970).

A number of difficulties with graphite as the source of the extinction were subsequently noted. Grain optics places a severe constraint on shape and size to account for the 217.5 nm feature (see Gilra (1972) and Hecht (1981) for a more complete analysis). Problems with the formation of crystalline graphite in the interstellar medium including the relevant properties of graphite are reviewed by Czyzak et al. (1982).

Of considerable current interest are the laboratory experiments on the quenched carbonaceous composites (QCC) produced by Sakata et al. (1983, 1984). A film was prepared by allowing the products of a microwave discharge in methane to condense on a quartz or NaCl substrate at room temperature. X-ray diffraction analysis revealed evidence for fine graphitic particles with some hydrogen present. The authors suggest the presence of hydrocarbons with conjugated double bonds. The infrared spectra of the film showed suggestive agreement with a number of observed infrared emission features.

A different explanation for the unidentified infrared emission bands and the long time mysterious diffuse interstellar bands is the proposal that they arise from polycyclic aromatic hydrocarbons (PAH's). The proposed infrared identification was due to Leger and Puget (1984), primarily based on laboratory spectra of coronene, a symmetric seven ring aromatic molecule.

Allamandola et al. (1985) showed that the Raman spectrum from auto exhaust compares well with the spectrum of the Orion bar in the 5-10 micron interval. The laboratory sample was a mixture of non-crystalline graphitic material and PAH's. Experiments on the residue composition from ethylene diffusion flames (Chakraborty and Long, 1968) determined the PAH concentration dependence on the oxygen and hydrogen concentration. Subsequently and simultaneously Leger and d'Hendecourt (1985) and van der Zwet and Allamandola (1985) pointed out that a correlation between visible aromatic spectra and the interstellar bands is to be expected but no identifications of bands were presented. The latter authors report experiments are under way to seek such comparisons.

Beginning about 1970 Sagan and Khare, summarized in their 1979 paper, have produced a variety of complex organic solids from cosmically abundant gases CH_4, C_2H_6, NH_3, H_2CO and H_2S. The products, produced by ultraviolet irradiation or spark discharge, are brown sticky films named tholins. They propose such material as constituents of the primitive oceans, aerosols in atmospheres of the outer planets and as being present in comets, carbonaceous chondrites and the interstellar medium.

Over the last decade or so Hoyle, Wickramasinghe and colleagues have investigated a variety of carbon compounds as the source of the interstellar extinction. Generally, they compared the infrared spectra of the material with the interstellar spectra. In a few cases the ultraviolet-visible spectrum was also determined and compared. This work is reviewed in a recent publications (Hoyle et al., 1985). Yabushita and Wada (1985) describe an attempt to reproduce the measurements on yeast and E. Coli made by Hoyle and colleagues. They found significant discrepancies between the two laboratories but pointed out the problems of exactly reproducing results. Yabushita and Wada emphasized the need to exactly specify the conditions under which the measurements are made. Moore and Donn (1983) also measured the infrared spectrum of E. Coli. In order to avoid the high pressures in preparing a KBr pellet they incorporated the E. Coli in a mull and reproduced the 3.4 micron feature. However, other absorption features, equally strong, at longer wavelengths than measured by Hoyle do not show up in the interstellar extinction.

d. Small Particles

Much of the existing data and many experiments deal with bulk properties and macroscopic material. This workshop is concerned with aggregates of matter below about one micron. Some proposals for grains have been as small as 5 nm where significant deviations from bulk behavior occur (Small Particles, 1977, 1981; Jortner, 1983; Rupin and Engelman, 1970).

There have been many laboratory programs to prepare and study a variety of characteristics of small particles. A number of these are described in the references in the preceding paragraph. Kamijo et al. (1975) present results for a number of refractory elements and oxides using the gas evaporation technique. References are given to other Japanese work in this area. Optical properties were not measured. Tables 1 and 2 include a number of similar experiments where the emphasis was on optical properties of the condensates.

Once particles are prepared the determination of size and composition for multielement grains becomes necessary. The characterization of particles by many different techniques is discussed in a National Bureau of Standards publication (Heinrich, 1980). Methods for the study of surfaces (Kane and Larrabee, 1974) and thin films are quite similar and may also be used. Many results and techniques for thin films can be found in the series "Physics of Thin Films, Advances in Research and Development." The initial stage of laying down a film consists of the formation of isolated aggregates.

4. Thermodynamic Data Including Vapor Pressures

Among the physical and chemical data found in the references in Section II, are extensive sets of thermodynamic properties of a variety of materials. In addition to those collections there are a number devoted to the subject of this section. Vapor pressures as a function of temperature are given by A. N. Nesmeianov (1963) for the elements and Baublik et al. (1984) for a large variety of compounds. The "Handbook of Chemistry and Physics" (Weast, 1985) revised about every year, gives constants for the vapor pressure equation of many compounds. Stull (1947) tabulates temperatures of organic compounds and inorganic compounds respectively at which the vapor pressure is 1, 5, 10, 30, 40, 60, 100, 200, 400, and 760 torr.

The most comprehensive collection of thermodynamic data appears to be the JANAF Thermochemical Tables (D. R. Stull and H. Prophet, 1971) published and updated by the Office of Standard Reference Data, U.S. National Bureau of Standards. The JANAF Tables give the temperature dependence for: heat capacity, entropy, Gibbs energy function $(F^o-H^o_{298})/T$, $H^o_T-H^o_{298}$, ΔH^o_f, ΔG^o_f, and log Kp. ΔH is the enthalpy, F or G is the Gibbs Free Energy and Kp is the equilibrium constant in units of atmospheres. The vapor pressure P is obtained from the equation:

$$\ln \Delta Fo_{vap} = -RT\ln P$$

Although the JANAF tables list ΔF in the next to last column, for interpolation purposes it is more accurate to use the Gibbs Function, $-(F^o_T-H^o_{298})/T$, which varies much more slowly with T. Then, ΔF_{vap} is given by:

$$F_{vap} = T\ [-(F^o_T-H^o_{298})/T]_{(cond)}-[-(F^o_T-H^o_{298})T + H^o_{f,298}\ (v)- H^o_{f,298}\ (cond)$$

$$\text{and } P_{vap} = \exp\ [-\ F_{(vap)}/RT]$$

where P_{vap} will be in atmospheres. Note that JANAF units are cal/molK for $-(F^o-H^o_{298})/T$ and Kcal/mole for $\Delta H^o_{f,298}$. The gas constant, R = 1.987 cal/mol. K.

The application is very straightforward for monatomic solids, for example, iron. For solids with complex compositions, as are all silicates, vaporization and stability can be discussed according to the treatment of Grossman and Larimer (1974). The reverse process (condensation) is more involved as discussed by Donn (1976, 1978, 1979) and at present no reliable procedure is available (Donn et al., 1981; Donn and Nuth, 1985). Extensive data for vapor pressures at low temperatures are given in the above collections. An additional source is found in Honig and Hook (1960).

III. EXPERIMENTAL INVESTIGATIONS OF GRAINS

1. Optics

In Section 2, data and some measurements on spherical and compact non-spherical particles were presented. This section deals with scattering on well defined, irregularly shaped grains.

One of the earliest studies was by Donn and Powell (1963) also Powell et al. (1967). The Angular scattering for both polarizations at two visible wavelengths were measured for micron size MgO cubes and ZnO fourlings. The latter have four symmetrically arranged narrow prongs extending from a central nucleus in the ideal case (which did not always occur). For the cubes, Mie calculations for a very similar distribution of spheres, gave a good match. However, with the fourlings, more large particles were needed and the measured scattering did not match either the angle or wavelength predictions.

More detailed and systematic investigations of scattering by irregular particles can be performed using microwaves and thereby scaling the particle dimension from microns to centimeters. An extensive program for this purpose was initiated by Greenberg (Wang and Greenberg, 1976; Greenberg and Gustafson, 1981). It was continued at The State University of New York at Albany (Schuerman, 1980a). The laboratory is currently run at the University of Florida, Gainesville. A similar laboratory has been operating at Ruhr University, Bochum, FRG (Zerull, 1980). Additional references to experiments on scattering by irregular particles, both optical and microwave, can be found in "Light Scattering by Irregularly Shaped Particles" (Schuerman, 1980b).

2. Sputtering

Sputtering of atoms or molecules off surfaces of either icy or refractory materials is an important process for grain evolution in a number of astronomical environments (e.g. Barlow; 1978). Experiments on sputtering by energetic ions have been carried out in several laboratories and results applied to astrophysical problems.

In the case of interstellar grains refractory "minerals", polymeric carbonaceous macromolecules and icy surfaces are likely to be involved. For solar system objects including satellites of the outer planets and cometary surfaces, volatile ice mixtures are the major constituents. Zodiacal and interplanetary dust and a large proportion of cometary grains will consist of refractory material. Barlow references sputtering experiments prior to about 1970. The basic techniques employ plasma discharges or ion beams to obtain the impacting ion. The ion beam method permits more quantitive measurements as the energy and angle of impact can be accurately controlled.

Detailed discussions and summaries of experimental results are given by Kaminsky (1965), Behrisch et al., (1973) and particularly Behrisch (1981, 1983). The last reference is a continuing series "Sputtering by Particle Bombardment". Volume I is subtitled "Single Element Compounds". Of considerable relevance is Chapter VII "Alloys and Compounds, Electrons and Neutrons, Surface Tomography". The chapter by Betz and Wehner, "Multicomponent Materials", provides data for a number of species of astrophysical importance. A third volume "Angular, Mass, Energy and Charge Distribution" is in preparation.

Sputtering produces a very complex structure on the irradiated surface. This is shown in the section on surface tomography in Behrisch (1983). The consequences for interstellar grains with regard to continuous exposure leading to destruction and for optical properties may be important. These experiments have been done on well ordered surfaces, the effect on amorphous surfaces and for grains under a micron in diameter need to be studied.

A brief but rather thorough review, with many references, to sputtering effects on condensed volatiles is given by Johnson et al. (1985). An additional very recent reference is the forthcoming proceedings of the NATO Conference on "Ices in the Solar System" edited by J. Klinger.

The active centers doing experiments in this area are at the University of Virginia (R. E. Johnson), Bell Laboratories (L. J. Lanzerotti), and the University of Catania in Italy (V. Pirronello).

3. Nucleation and Condensation

A number of calculations of grain formation in stellar atmospheres and circumstellar shells have been carried out over the past two decades (see Donn and Nuth, 1985 for references). The assumptions used in these investigations have been questioned by Donn in a series of papers, including the reference above. An experimental study of the condensation of refractory materials at temperatures in the range 750-1200K was undertaken at the Goddard Space Flight Center to study this problem (see Donn and Nuth, 1985 for references). In these experiments the reactant or reactants were thermally vaporized to form a cloud at a known temperature within which particles condensed. An inherent difficulty with this technique is the attainment of good mixing in the vapor phase with multi component mixtures. These experiments were an extension of those described in Section IIc for the preparation of synthetic silicate grains. For a variety of other purposes, the problem of the condensation of refractory materials has been investigated at a number of other institutions using different techniques, primarily employing shock tubes. These have all been referenced and very briefly described by Donn and Nuth. In all cases the experiments resulted in significant disagreement with nucleation theory.

At Goddard, plans have been developed for studying both nucleation and particle formation from multicomponent gases in a flow system. The separate components will be mixed in a high temperature furnace where condensation cannot occur. The now well mixed gas will flow into a variable, lower temperature furnace and condense under controlled conditions.

4. Clusters

The proposal that nucleation theory cannot handle mutlicomponent mixtures (Donn, 1976) was based on the formation of metastable clusters that affect the final grain composition. Several of the condensation experiments referenced in the last Section yielded particles with non-equilibrium composition (Nuth and Donn, 1982, 1983; Stephens and Bauer, 1985).

In order to study the condensation process and determine thermodynamic and kinetic data for developing a kinetic theory of condensation an investigation of the precondensation clusters is an important procedure. In recent years there has been extensive research into the properties of clusters, largely because of their role as catalysts. This work is well presented in several conference proceedings ("Experiments on Clusters", 1984; Gole and Stwalley, 1982; Borel and Buttet, 1981). Gas phase cluster experiments for the most part involved single species, often metallic or in several cases alkali halides. In all instances the cluster formed by expansion and cooling of the carrier gas plus condensible species so that the temperature-pressure conditions of cluster formation were not determined.

In the last two years two procedures with considerable astrophysical significance have been applied to the investigation of clusters. Instead of using an inert ambient carrier, a small concentration of reactant is introduced into the flowing carrier. By this means reactions of cobalt and niobium clusters with hydrogen (Guesir et al., 1985) and iron with molecular hydrogen (Ricktsmeier et al., 1985) were studied. With all three cluster types, the reactivity was a strong function of cluster size. Whetten et al. (1985) reacted iron clusters with O_2, H_2S, and CH_4. In all cases atomic iron is unreactive, the reactivity of iron clusters tends to increase with cluster size and levels off for the larger clusters. CH_4 did not react with iron clusters.

By vaporizing arsenic or cesium with sulfur, Martin (1984a, 1984b) obtained mixed clusters with a wide range of composition ratios. In these experiments the two species were vaporized from adjacent crucibles (Cs + S) or as arsenic sulfide from a single crucible. Reactant gases were also introduced into the helium carrier. Research in the new area of cluster reactivity and composite clusters is very active and new results are continually reported.

An experimental program on clusters aimed at the astrophysical problem of grain formation has been undertaken at Goddard (Donn et al., 1981). The emphasis will be on the formation of silicate grains composed of cosmically abundant metals. The plan is to create and then condense multicomponent vapor mixtures. The composition of the vapor, temperature and pressure of cluster formation are the basic parameters to be varied in the experiment. The size and compositional distribution as a function of temperature are the results to be measured. This information will be a major contribution to the understanding of cosmic grain formation.

5. Low Temperature Experiments

1. Matrix Isolation

There is always a question of organization in a review covering a broad area of research - How best to present material which overlaps several sections? In the present instance clustering has been studied using high temperature vaporization as in Section III-1 and also in low temperature matrices. The latter aspect is considered here.

There is a rather long history of the study of clustering and reactivity in matrices. The general techniques are reviewed by Moskovits and Ozin (1976) and examples appear in Gole and Stwalley (1982). Primarily spectroscopic applications are given by Meyer (1971). Two reviews emphasizing the study of molecules prepared at high temperatures have been written by Weltner (1967, 1969). He has also studied small carbon clusters in inert matrices (Weltner 1964a, b, 1966, 1976). Kratschmer et al. (1985) deposited carbon vapor at 10K and warmed up the film while monitoring the spectrum. They obtained results which may be compared with several diffuse interstellar bands.

Wdowiak (1980) has condensed the discharge products of methane-argon mixtures at 10K and examined the visible spectrum as a function of time and ultraviolet bleaching. Suggestive similarities with diffuse bands occurred in these experiments also. Khanna et al. (1981) monitored changes in the spectra of SiO in N_2 with warmup. In addition to the growth of small polymers of SiO, they obtained a non-volatile residue that had an absorption similar to that of the Si_2O_3 particles that characterize condensates from SiO vapor. Similar results were obtained for Mg + SiO gas mixtures (Donn et al. 1981). Experiments were also carried out on Fe + SiO again with similar results.

2. Water Ice and Ice Mixtures

A different phase of low temperature research applicable to astrophysical problems is the study of condensed volatile species. This aspect deals with pure water ice and simulated cosmic ice mixtures.

A number of laboratory studies of the spectra of ices and ice mixtures has been carried out. Lebofsky and Fegley (1976) have provided the reflection spectra of several molecular frosts in the wavelength range 0.3-1 micron. Moore (1981) also shows the spectra from 2.5-15 microns of a variety of condensed molecules and mixtures. A similar collection of spectra was presented by Hagen et al. (1983) which includes the effect of changing concentration and temperature (permitting increasing degrees of diffusion in the sample). The spectra of hydrated frosts, over the wavelength range from 1-6 microns, has been studied by Smythe (1975).

A number of experiments have investigated the infrared spectrum of amorphous ice and applied the results to astronomical observations (Hagen et al., 1981; Leger et al., 1983, Kitta and Kratschmer, 1983). Extensive physiochemical experiments have been carried out on amorphous ice. These are reviewed by Sceats and Rice (1982).

In addition to water ice and ice mixtures, gas hydrates or clathrate hydrates have been proposed for interstellar grains or grain mantles although most of the emphasis of these experiments have been for comets. Miller (1961, 1973) reports experimental results for astrophysically interesting clathrates. Extensive reviews are given by Davidson (1973) and by van der Waals and Platteeuw (1959). Recent results are given by Cady (1983) and Davidson et al. (1984). An inability to directly condense clathrates below about 100K has been demonstrated and briefly discussed by Bertie and Devlin (1983).

A comprehensive presentation of the physics and chemistry of water, ice and aqueous solutions can be found in the series "Water - A Comprehensive Treatise" edited by Frank. Recent research on ice appears in the proceedings of the symposia "The Physics and Chemistry of Ice" (Riehl et al., 1969), (Whalley et al., 1973), (J. of Glaciology, 1978) and the volume for the 1983 meeting.

Because matter in space is irradiated by ultraviolet photons and particles in the Kev or Mev range, experiments on ice irradiation have been carried out. A systematic program on ultraviolet irradiation of ice mixtures has been underway at Leiden University. An account of this work and many references to it are given in Greenberg (1982). At Goddard, the effect of 1 Mev protons on ice mixtures has been studied (Moore and Donn, 1983). At the Joffe Institute of Physics and Technology in Leningrad, experiments on the irradiation (Kaimakov et al., 1977) and vaporization of ice and ice-dust mixtures (Kaimakov and Sharkey, 1972; Lizunkova et al., 1977) have been carried out. Experiments on the photodetachment, photodissociation and photochémistry of ice mixtures have recently been performed at the Institute for Molecular Sciences in Japan (Nishi et al., 1984).

The references to experimental investigations have been colored by my interests. As pointed out in the beginning, this review is far from complete. A number of significant procedures are undoubtedly missing and important experimental studies are also omitted when particular techniques are mentioned. I apologize to the reader who may be misled by the first omission and to the investigators who were not given due credit by the second. Some of these deficiencies would have been avoided had I been able to attend this stimulating meeting but others were due to a desire to limit the size of the present work and to guide the reader to sources of data and additional references.

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