

Section II

Laboratory Studies and Simulations

PHYSICAL PROPERTIES OF FROZEN VOLATILES—THEIR RELEVANCE TO THE STUDY OF COMET NUCLEI

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ABSTRACT. The structural and thermodynamical properties of water ice and ice mixtures containing CO, CO₂, CH₄, and NH₃ are thought to be important for the evolution of cometary nuclei. Based on recent laboratory studies performed by several groups, an overview is given of the properties of various ices condensed at low temperatures and of their evolution during heating up to a temperature of about 200 K, typical of the perihelion temperature of a comet such as P/Halley. It is shown that the porous surface of amorphous water ice plays an important role in the retention of other volatiles. The kinetics of formation and of decomposition of clathrate hydrates are discussed. The molecular hydrates formed by NH₃ are briefly presented, and the possibility of their occurrence in comet nuclei is discussed. With special attention drawn to amorphous ices and clathrate hydrates, a qualitative discussion of the influence of the physical properties of various types of ices on the thermal behavior of comet nuclei and on gas production rates of comets is presented.

1. Introduction

The first hint that the evaporation of ices might be responsible for the well-known cometary phenomena is found in the book *Exposition du Système du Monde*, by Pierre Simon de Laplace (1796). But, as it became more and more evident during the second half of the 19th century that meteor streams were related to the orbits of comets, the idea of Laplace was forgotten, and comets were thought to be made of meteoritic debris that had adsorbed a certain amount of gas. It was Fred Whipple (1950) who, with his "icy conglomerate model," achieved the decisive path toward a modern concept of comet nuclei. Then, in order to explain the simultaneous outgassing of species with very different vapor pressures, Delsemme and Swings (1952) proposed that the frozen volatiles should be present in the form of clathrate hydrates.

Watson et al. (1963) have studied the sublimation of different kinds of ices from objects orbiting in the Solar System. For water-ice spheres of 1-km radius in the orbits of some prominent comets, the authors found lifetimes ranging from less than 10⁵ years

(Encke, Grigg-Skjellerup, Tempel 2, Pons-Winnecke, Forbes, Kopff, Giacobini-Zinner, d'Arrest, Daniel, Faye, Schaumasse, Tuttle 1, Crommelin, Pons-Brooks, and Halley) to more than 10^9 years (Schwassmann-Wachmann 1).

Donn (1963) pointed out that the fact that comets contain ices more volatile than H_2O necessarily implies that comets have been accreted at low velocities. He gave a value of ≈ 0.1 km/s as a maximum relative velocity of accreting particles. He found that the density of a comet formed under these conditions should not exceed 450 kg/m^3 , even if compaction due to self-gravitation of an ice body with a 10-km radius is taken into account.

After these pioneering studies, until the 1970s, very little progress was made in improving our understanding of the physics and chemistry of comet nuclei. The reason is obvious: No direct observations of comet nuclei were available until the recent space missions to Comet Halley. Further, a great number of the spectroscopically detectable chemical species are products of photolytical processes that occur in the coma. Thus, the determination of the mother molecules present in the nucleus is extremely difficult.

Progress in laboratory studies during the late 1960s and the 1970s (McMillan and Los 1965, Ghormley 1967, 1968, Delsemme and Wenger 1970, and Narten et al. 1976) reactivated the discussion on physical properties of cometary ices (see also Delsemme and Miller 1970, Patashnick et al. 1974, and Whipple and Huebner 1976). The most decisive advance in our understanding of cometary phenomena came from the recent observational campaign of Comet P/Halley. The observational evidence accumulated during this opportunity gave us input for the development of more realistic comet models and stimulated laboratory work on physico-chemical processes that might be relevant for comet nuclei.

An important finding was the low average density of the nucleus (280 to 650 kg/m^3) (Rickman 1989). These values fit well the estimation by Donn mentioned above, as well as that by Greenberg (1986) based on considerations of the agglomeration of interstellar grain-mantle particles.

We can now definitively conclude that H_2O is the major volatile component of comets. For several minor constituents, estimates of their abundances are now available.

Based on data from the Giotto Neutral Mass Spectrometer, the abundances of CO and N_2 have been estimated to be lower than 7% and 10%, respectively, compared with that of H_2O (Eberhardt et al. 1987). The CO/ H_2O ratio deduced from data from the International Ultraviolet Explorer (IUE) satellite is in the range of 0.1 to 0.2 (Festou et al. 1986). For NH_3 and CH_4 , best fits of the Giotto Ion Mass Spectrometer data are obtained with ratios of 0.01 to 0.02 and 0.02, respectively (Allen et al. 1987). CH_4 also has been detected by Drapatz et al. (1987), using a Fourier Transform spectrometer. From the emission band strengths of NH_2 , Wyckoff et al. (1988) deduced an ammonia abundance of 0.005 with respect to water in the coma of Comet Halley. Based on infrared (IR) spectra from the InfraKrasnoi Spectrometre (IKS) on board VEGA 1, the CO_2/H_2O ratio is thought to be on the order of 0.02 (Moroz et al. 1987). HCN has been detected with the 13.7-m radio-telescope of the Five College Radio Astronomy Observatory (Schloerb et al. 1987) and with the 30-m radio-telescope of the Institut de Radio-Astronomie Millimétrique (IRAM) (Bockelée-Morvan et al. 1986). The very unstable radical S_2 has been detected in comets (A'Hearn and Feldman 1985), thus indicating a very low formation temperature of comet nuclei.

As water is the most abundant volatile component of comets, this review focuses on the properties of water-rich components containing a more or less important amount of

other astrophysically relevant volatile substances. Chemical alterations of icy materials are deliberately excluded. Nevertheless, it should be mentioned that the action of ultraviolet radiation and, to some extent, of cosmic rays certainly has produced major chemical changes in the icy material of comets.

2. Ices and Ice Mixtures Relevant to Comets

2.1. DIFFERENT FORMS OF WATER ICE

Several monographs and conference proceedings exist that are partially or completely dedicated to the physical properties of water ice. See, for example, Eisenberg and Kauzmann (1969), Riehl et al. (1969), Whalley et al. (1973), Hobbs (1974), and special issues of the *Journal of Glaciology* (1978), *Journal of Physical Chemistry* (1983), and *Journal de Physique* (1987). The book *Ices in the Solar System*, edited by Klinger et al. (1985a), is currently the only book exclusively dedicated to ices in astrophysical environments.

The basis of any solid H₂O structure is the water molecule. It is composed of one oxygen atom that is associated with two hydrogen atoms that form a valence angle of 104.5°. When an ice structure is built up with individual water molecules, the oxygen atom of one water molecule can be considered as the center of a regular tetrahedron, the angles of which are occupied by other oxygen atoms. The continuity of the crystal structure requires that every oxygen atom on the summit of a tetrahedron can itself be regarded as the center of another tetrahedron, oriented upside down with respect to the first one. Depending on the azimuthal orientation of the second tetrahedron with respect to the first, the crystal structure obtained is hexagonal (the angles of the tetrahedra are superposed) or cubic (the second tetrahedron is rotated by an angle of 60°). If no long-range correlation exists between the orientations of the basic tetrahedra, the ice is amorphous.

When the bond angles between water molecules are distorted, a great number of new ice structures (more than 10) can be obtained. At temperatures near 273 K, pressures as high as 0.2 GPa are needed to produce one of these phases (ice II). But some of these high-pressure phases are metastable at liquid-nitrogen temperature.

2.1.1. Hexagonal Ice. Hexagonal ice (space group P6₃/mmc) is the most stable and most common form of ice. It is generally considered to be the only naturally occurring phase of water ice on Earth. It is obtained by freezing liquid water as well as by condensing water vapor on a substrate at a temperature higher than 150 K. It can also be obtained by phase transitions from other forms of ice.

2.1.2. Cubic Ice. Cubic ice (space group F $\bar{4}$ 3m) is obtained by condensation of water vapor on a substrate at a temperature between 110 and 150 K. At 200 K, cubic ice irreversibly transforms to hexagonal ice. The change in enthalpy during the recrystallization has been measured by McMillan and Los (1965) and by Sugisaki et al. (1968) as 160 J/mole, whereas Ghormley (1968) finds it to be less than 20 J/mole.

For a long time, the question was open about whether cubic ice could be formed from the liquid phase. The first argument in favor of a formation from the liquid was given by Whalley (1981). In fact, since the 17th century, a small number of observations of a

28° halo, called Scheiner's halo, around the Sun or the Moon have been reported. Whalley (1981) pointed out that this phenomenon is compatible with a refraction under minimum deviation on the octahedral faces of crystals of cubic ice. As, in the atmosphere, ice crystals form from supercooled droplets of water, the conclusion is that cubic ice should be able to form from the liquid. In the meantime, Mayer and Hallbrucker (1987) succeeded in producing cubic ice from water droplets of about 3 μm in diameter.

2.1.3. Amorphous Ice. Amorphous ice is formed by vapor deposition at temperatures lower than 100 K. A structural model of amorphous ice has been published by Boutron and Alben (1975). These authors considered a random network of tetrahedrally bonded atoms. This model seems consistent with neutron diffraction studies by Chowdhury et al. (1983). But obviously amorphous ice cannot be defined uniquely from a structural point of view. Its characteristics can change depending on the conditions of formation (deposition temperature and deposition rate). Narten et al. (1976) showed that there exist at least two different forms of amorphous ice, with important differences in density and in nearest neighbor distribution. Laufer et al. (1987) also concluded, from gas trapping experiments, that at least two forms of amorphous ice exist. From measurements of the vapor pressure of H_2O , Kouchi (1989) concluded that three forms of amorphous ice (phases I, II, and III) exist. The author suggests that forms I and III are more stable than form II. The existence of superdense amorphous ice found by Delsemme and Wenger (1970) has not been confirmed by other studies.

The IR absorption spectrum of amorphous ice is characterized by a broadening of the OH stretching band situated at 3.1 μm (Léger et al. 1979). The libration band, which is situated at 11.8 μm for crystalline ice, is broader and shallower for amorphous ice. The absorption maximum is shifted to 12.5 μm . The third important absorption band corresponds to an optical mode of molecular displacement at $\lambda \approx 45 \mu\text{m}$. This band is very different for amorphous ice than it is for crystalline ice (Léger et al. 1983). The differences in the IR spectra between amorphous and crystalline ice have made it possible to identify amorphous ice in molecular clouds (see, for example, Papoular et al. 1978).

Amorphous ice is characterized by a large specific surface area (several hundreds of square meters per gram). Adsorption studies revealed a significant microporosity (Mayer and Pletzer 1987 and Schmitt et al. 1987). The large specific surface area and the microporosity are likely to be important for the retention of substances more volatile than H_2O in cometary ices.

During heating, amorphous ice irreversibly transforms to cubic ice. The transition temperatures given in the literature vary between 113 K (Dowell and Rinfret 1960) and 153 K (Ghormley 1968, and Mayer and Pletzer 1984, 1985). Schmitt et al. (1989a) studied the crystallization of ice condensed at 10 K. From the modification of the 3.1- μm IR absorption band, these authors derived an activation law for the crystallization as:

$$\tau = A \cdot \exp(-E_A/kT) \quad (1)$$

with $A = 9.54 \times 10^{-14}$ s and $-E_A/k = 5370$ K. In Equation (1), τ is not a time constant in the usual sense, but is rather the time needed to make the 3.1- μm absorption band indistinguishable from that of crystalline ice.

During the crystallization of the amorphous ice, the specific surface area of the samples is reduced by about a factor of 100 (Ocampo and Klinger 1982).

We expect a very low heat conduction coefficient for amorphous ice, as for all amorphous solids (Klinger 1980). Further, the heat conduction coefficients of amorphous solids decrease when the temperature is lowered. The reverse is true for crystalline solids.

Recently, measurements of the vapor pressure of amorphous ice have been made by Kouchi (1987). According to this work, the vapor pressure of amorphous ice is found to be one or two orders of magnitude larger than that of crystalline ice at the same temperature. The condensation temperature of the ice strongly influences the value of the vapor pressure.

It must be said that the capability to form an amorphous solid when gas is slowly deposited at low temperatures is not restricted to H₂O. We can say as a general rule that an amorphous solid is formed when the potential barrier for bringing the adsorbed molecules into an energetically favorable position is too high compared with the temperature of the substrate and when the deposition rate is sufficiently low to prevent local heating due to the adsorption of the molecules. In particular, CO₂ deposited at 10 K (Falk 1987) and CO at the same temperature (Kouchi 1989) are known to form amorphous solids.

2.2. CLATHRATE HYDRATES

Clathrate hydrates are formed of a crystal lattice of water molecules. This lattice contains cages of different sizes able to entrap gas molecules. For several years, two cubic structures (structures I and II) and a tetragonal structure have been known. The only known gases that form tetragonal hydrates are Br₂ and dimethyl ether (Miller 1985). Recently, a new structure has been discovered (Ripmeester et al. 1987). For a given molecule, the type of structure formed essentially depends on the size of the molecule. The formation of mixed hydrates containing different molecular species is possible. The encaged molecules are weakly bonded to the lattice by van der Waals forces and thus are rather mobile between adjacent cages. A complete filling of all available cages is thermodynamically impossible, but a rather high degree of cage occupancy is possible. It must be said that the guest molecules are necessary to stabilize the clathrate lattice.

A great number of astrophysically relevant atoms and molecules do form clathrate hydrates. In particular, this is the case for CO, CO₂, CH₄, C₂H₆, H₂S, SO₂, N₂, O₂, Ar, Kr, and Xe. The phase diagram of some of these clathrate hydrates is shown in Figure 1. The existence of CO hydrate has been predicted for a long time, but found only recently. Bar-Nun et al. (1985) studied the trapping and release of different gases by water and suggested that CO clathrate hydrate might have been formed. In a more recent study, Kouchi (1989), using electron diffraction, examined a CO/H₂O condensate obtained in the same way as Bar-Nun et al. (1985) had obtained theirs. Kouchi found no evidence for the formation of CO clathrate. Nevertheless, in the meantime, the formal proof of the existence of this hydrate has been established by Davidson et al. (1987a). These authors showed by X-ray diffraction studies that CO formed a clathrate of structure I. The phase diagram of this hydrate has not yet been measured in detail. The dissociation pressure at 273 K was found to be 12.8±2 MPa (Davidson et al. 1987b).

The reason why He and Ne clathrates have not been found seems to be that these atoms are too small to stabilize the clathrate lattice. In fact, it has been shown by Kahane et al. (1969) that He and Ne are able to diffuse interstitially through the lattice of hexagonal ice. Recently, it has been found by Londono et al. (1988) that a helium hydrate with the

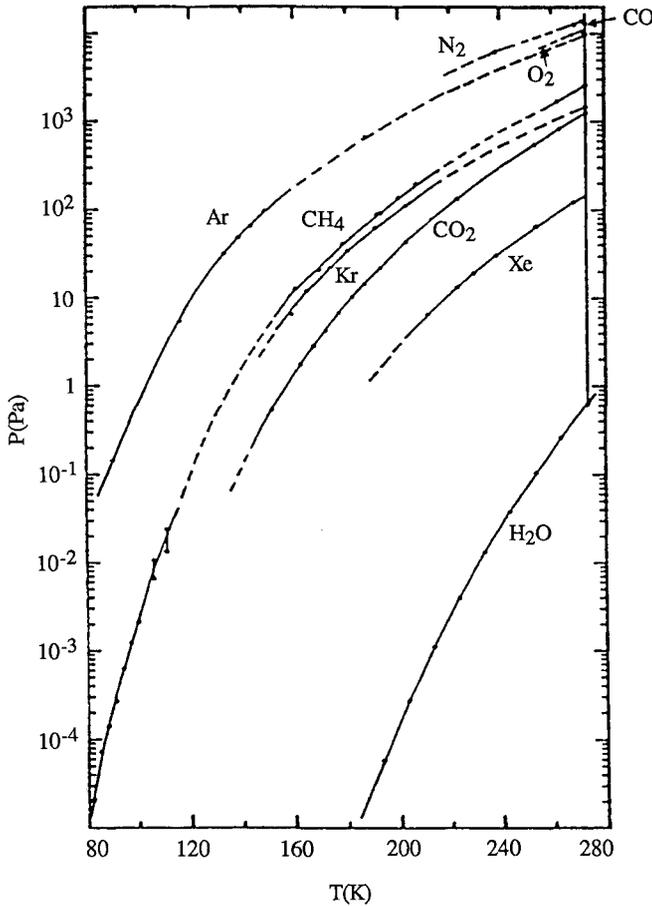


Figure 1. Dissociation pressure of some clathrate hydrates (after Schmitt et al. 1989b).

structure of one of the high-pressure forms of ice (ice III) can be prepared. At a temperature on the order of 252 K, the dissociation pressure of the hydrate is 0.28 GPa.

It should be mentioned here that virtually all experimental work on astrophysically relevant clathrate hydrates has been done at temperatures higher than 100 K. Taking into account that H₂O condensed at temperatures lower than 100 K forms an amorphous solid, it is questionable whether a clathrate hydrate lattice can be built up at temperatures much lower than 100 K. The occurrence of clathrate hydrates in comets is discussed in more detail in Section 3.1.

2.3. MOLECULAR HYDRATES

Among the compounds that form molecular hydrates, a very important one for the studies of comets is NH_3 . A study of the phase diagram of the water-rich region of the system $\text{H}_2\text{O}-\text{NH}_3$ has been published by Johnson et al. (1985). For obvious reasons, most of the studies of this system have been done starting with a solution of ammonia in water.

Bertie and Morrison (1980) have studied the IR spectra of $\text{NH}_3\cdot\text{H}_2\text{O}$ and of $2\text{NH}_3\cdot\text{H}_2\text{O}$. The structure and the IR spectrum of $\text{NH}_3\cdot 2\text{H}_2\text{O}$ have been investigated by Bertie and Shehata (1984).

2.4. EVOLUTION OF ICE MIXTURES CONDENSED AT LOW TEMPERATURES

Several groups have studied the evolution of ice mixtures containing H_2O and other components. These ice mixtures have been obtained by codeposition at temperatures between 10 and 100 K or by the trapping of gas in a preexisting water ice matrix (see, for example, Bar-Nun et al. 1985, Bar-Nun et al. 1987, Bar-Nun et al. 1988, Kouchi 1989, Laufer et al. 1987, Sandford and Allamandola 1988, and Schmitt et al. 1988).

There seems to be a general agreement among all these studies that volatiles can remain trapped in the water-ice matrix up to temperatures much higher than the normal sublimation temperature. Some discrepancy still seems to exist concerning the temperature up to which the volatiles can be retained and on the amount of trapped volatiles.

Bar-Nun et al. (1985) investigated the trapping and release of H_2 , CO , CO_2 , CH_4 , Ar, Ne, and N_2 from 16 K upward. CO , CH_4 , Ar, and N_2 were released in three or four temperature ranges. The authors interpreted every phase of gas release in terms of a different trapping mechanism. Between 30 and 55 K, the frozen gases sublimate freely. Between 135 and 155 K, the gas trapped in the amorphous ice matrix is released. The release between 165 and 190 K that is accompanied by a production of water vapor is explained by the dissociation of clathrate hydrates. The outgassing that is occasionally found between 160 and 175 K is attributed to the recrystallization from cubic to hexagonal ice. It should be mentioned that, during these experiments, the partial pressure of the different constituents was measured using a mass spectrometer. Concerning the quantity of trapped gas, these authors reported that water ice could trap volatiles in quantities considerably larger than 1:1. More recently, Bar-Nun et al. (1988) studied the trapping of gases by water ice in the range of 24 to 100 K. Between 50 and 75 K, they found a decrease of the quantity trapped going from CH_4 to CO to N_2 to Ar.

Very different results have been obtained by Schmitt et al. (1988). These authors directly monitored the quantity of trapped gas present in the solid by means of IR spectroscopy. Their samples were obtained by codeposition at about 10 K. For $\text{CO}:\text{H}_2\text{O}$, the CO evaporation starts at 25 K. When a temperature of 50 K is reached, the $\text{CO}/\text{H}_2\text{O}$ ratio is invariably found to be about 0.1, regardless of the initial concentration. Between 50 and 110 K, the CO decrease is very slow (about 1% per day at 110 K). When 135 K is reached, the remaining CO completely disappears from the solid. This CO disappearance seems directly related to the crystallization of the water ice (Schmitt et al. 1989b).

A mixture of $\text{CH}_4:\text{H}_2\text{O}$ shows a similar behavior, but the onset of the first evaporation phase is observed at 35 K.

In the case of CO₂:H₂O, a small amount of evaporation is found at 60 K. In a sample of 5- μ m thickness, 10 days are needed for the complete removal of the CO₂ at 127 K.

NH₃:H₂O has a very different behavior. NH₃ remains in the H₂O matrix up to temperatures as high as 170 K. It evaporates only slightly before H₂O does. The reason seems to be that ammonia forms a hydrate at about 140 K.

Sandford and Allamandola (1988) also studied the condensation and vaporization behavior of CO:H₂O ices by IR spectroscopy in the solid. They found an outgassing behavior similar to that found by Bar-Nun et al. (1985).

Recently, Kouchi (1989) investigated the system CO—H₂O. In this study, the vapor pressure of CO was measured, and the outgassing studied by monitoring the gas phase with a mass spectrometer. It has been reported that CO, condensed with a deposition rate lower than 100 nm/hr, forms an amorphous solid. When the deposition rate is higher, crystalline CO is formed even at 10 K. The vapor pressure for amorphous CO is found to be one order of magnitude higher than that for crystalline ice. Concerning the evaporation of CO—H₂O ice, the CO was found to escape in seven different ranges. The first range, which starts at 14 K, is explained by the sublimation of amorphous CO. The second starts at 24 K and is thought to be due to the evaporation of the crystalline α -phase of CO. The escape of CO that starts at 34 K is explained by the desorption of CO adsorbed on amorphous ice. Unlike Sandford and Allamandola (1988), Kouchi (1989) excluded the possibility of CO accretion on ice up to temperatures as high as 50 K. A small peak of CO outgassing is attributed to the onset of evaporation of amorphous H₂O. An important CO peak obviously is associated with the crystallization of amorphous H₂O. Only two very small CO peaks are found in the range between 155 and 165 K. These peaks are two orders of magnitude lower than that of the water peak in this range. As stated earlier, no evidence was found for the occurrence of CO clathrate.

Up to now, no final conclusion could be given concerning the discrepancies mentioned earlier, especially concerning outgassing in the high-temperature range. If the thickness of the samples used is important, we can think about the trapping mechanisms responsible for the high-temperature outgassing. Two possibilities exist: First, the trapping is due to a microphysical process (trapping in grain boundaries or in interstitial or substitutional positions in the H₂O lattice). Second, the trapping is due to a bubble formation in the water-ice matrix. If a microphysical process is responsible for this phenomenon, this means that it must be possible to characterize the outgassing by a diffusion coefficient as a function of temperature. Such an investigation has not yet been successfully carried out. If the gas is trapped in bubbles, it is rather easy to estimate the required gas pressure at a given temperature for a given quantity of trapped gas. Such estimates lead to pressures as high as several MPa (Schmitt et al. 1988). It is questionable whether the ice matrix could withstand such pressures.

3. Discussion

Now that we have reviewed some important properties of water ices and ice mixtures dominated by water, let us discuss the insight into cometary physics that can give us the knowledge of these properties.

According to recent data on the average density of comet nuclei (Rickman 1989), we have to consider comets as fluffy aggregates containing a dust component and a rather complex ice component.

3.1. CLATHRATE AND MOLECULAR HYDRATES IN COMETS

3.1.1. *Clathrate Hydrates.* On the basis of our knowledge of clathrate hydrates, it is not possible to establish whether or not comets contain them. But let us recall that we have good arguments for a direct formation of comets from cold ($\ll 100$ K) interstellar grains (the fluffiness of cometary material, presence of S_2 , and low albedo). Thus, we can affirm that clathrate hydrates were not initially present in comet nuclei. The reason is that there is no evidence that low-temperature binary or multicomponent deposits can reorganize to form clathrate structures. Let us remember that the extrapolation to lower temperatures of the activation law of Schmitt et al. (1989a) (Equation (1)) gives a stability of amorphous ice at 75 K (condensed at 10 K) of about ten times the age of the Solar System.

Nevertheless, clathrate hydrates can be formed when comets enter the inner parts of the Solar system, but only under two conditions:

1. The ice layers involved in clathration must be heated sufficiently, up to temperatures higher than 100 K.
2. The confinement of the clathrate-forming ice must be sufficiently efficient to allow the system to exceed the dissociation pressure of the clathrate.

The more the ice is heated, the faster the reaction is and the better the pressure confinement must be. Such confinement is quite unlikely in a porous system such as comets are thought to be.

A special problem is that of CO_2 clathrate. As supposed for a long time (Miller 1973), CO_2 clathrate has been proved to be unstable at temperatures lower than 120 K (Davidson et al. 1984). Smoluchowski (1988) pointed out that the decomposition of CO_2 clathrate during cooling of the comet nucleus after the perihelion passage could lead to an important brittleness of the nucleus.

Based on experimental results of clathrate formation and decomposition, Klinger et al. (1985b) showed that there is no way to explain the simultaneous outgassing of substances with very different volatility by the decomposition of clathrate hydrates. The reason is that the clathrate lattice collapses to an ice structure when the stabilizing host molecule diffuses out. This means that the more volatile species would be lost well before the water of the guest lattice.

In the same paper, the authors proposed an alternative explanation for the simultaneous outgassing of different volatile species: suppose that the comet nucleus is a porous medium. When the nucleus approaches the Sun, the surface will be heated, and a thermal gradient will be established in the subsurface layers. The local temperature then governs the sublimation of ices more volatile than H_2O in these layers. These volatiles escape to the surface and can mix with H_2O that sublimates on the surface. Thus, any mixing ratio can be obtained in the coma. Recent model calculations by Espinasse et al. (1989) have demonstrated that this concept is viable.

3.1.2. *Molecular Hydrates.* Molecular hydrates behave very differently than do clathrate hydrates. The molecular hydrates form very stable hydrogen bonds and are likely to evaporate simultaneously with the ice matrix. It has been pointed out by Schmitt and

Klinger (1987) that the outgassing ratio of a given volatile species with respect to H₂O could be diagnostic of the volatility of the mother molecules. A constant outgassing of a given species with respect to the H₂O production over an important part of the orbit of a comet indicates that the mother molecule has a low volatility. On the other hand, a variable outgassing ratio indicates that the corresponding mother molecule is highly volatile. One type of mother molecule with low volatility could be molecular hydrates. As stated earlier, NH₃ was found to form a hydrate if the ammonia-containing ice layer was heated up to 140 K.

3.2. ICES AND THE INTERNAL EVOLUTION OF COMETS

The possibility of an internal evolution of comets has been neglected for a long time. The knowledge that we now have on the rather complex physico-chemical processes that occur in low-temperature condensates, combined with the concept of a very fluffy nucleus, sheds new light on this problem. Smoluchowski (1985) pointed out that the gas phase within the pores of the nucleus might contribute in an important manner to the heat transport in the interior of the nucleus. He also suggested that volatiles could be able to recondense in colder layers of the nucleus. Klinger (1986) proposed that such kinds of sublimation-recondensation processes are likely to produce isotope fractionations.

During the Kometensimulation (KOSI, "comet simulation experiment"), the realism of all these phenomena was illustrated (see Klinger et al. 1989a, 1989b, and Spohn et al. 1989). Both the heat transport due to the vapor phase and the chemical differentiation due to the phase transition of amorphous to cubic ice and to sublimation-recondensation processes appear in the comet model developed by Espinasse et al. (1989).

4. Conclusion

Important progress has been made in the study of different types of icy systems that are likely to be relevant to comets and to their evolution as a function of temperature. These results, combined with adequate modeling, are likely to make us better understand the physics of comet nuclei.

The major problem that we have to face is how to use observational data to constrain the model predictions based on laboratory studies. The best way to do this would be to monitor the production rates of different volatile species over long portions of the orbits of different comets.

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