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FORMATION AND DECOMPOSITION OF ICY CLATHRATES

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Abstract: Recent experimental studies (1) of the formation and decomposition of \( \text{CO}_2 \) - clathrates, from and into \( \text{H}_2\text{O} \) - ice and \( \text{CO}_2 \), seem to indicate an extremely low apparent activation energy (2) for these processes. A rough estimate of the probable energy associated with volume diffusion of \( \text{CO}_2 \) molecule through hexagonal openings in the clathrate cage has been made. It suggests that these reactions occur primarily on surfaces of ice grains. The observed suppression of decomposition of clathrates by pressure (3) is in qualitative agreement with these conclusions. These and earlier results (4) indicate that porosity of cometary nuclei should play an important role in affecting the rate of escape of the entrapped molecules into the cometary coma.

References

(2) Smoluchowski R., EOS Nov. 12 (1985).

COMMENTS

Name of Speaker : E. WHALLEY for SMOLUCHOWSKI

J. P. DEVLIN

Relative to Prof. Glen's request for comment on formation of the empty clathrate hydrate, I believe that non polar guest molecules in thin deposite offer the hope of seeing this in the \( \sim 120 \) K range. We have observed that warming of a 6 micron thick \( \text{H}_2\text{O} \) hydrate into the \( 140 \) K range causes the HOD O-D stretch band to move to a position between the \( 2425 \) cm\(^{-1} \) hydrate value and the \( 2410 \) cm\(^{-1} \) ice value (10K values). However, the sharpness of the band resembled ice Ic and leads us to believe it was not the empty clathrate structure.

Name of Speaker : E. WHALLEY for SMOLUCHOWSKI

J.W. GLEN

Is it known what happens to a clathrate hydrate when it is cooled to a low temperature and then placed in a low-pressure environnement ? Do the guest molecules leave ? If so what happens to the cage structure ? Does it survive in the same way as the high pressure phases of ice at low temperature ? If not does it become amorphous ? Does this not have important implications for the behaviour of clathrates in astrophysical situations such as those discussed by Dr. Smoluchowski ? If the cage does survive it might be most interesting to measure its thermal...
properties in the light of Dr. Whites' explanation of the thermal properties of clathrates.

Answer by M.A.WHITIE:

It has been found that pumping on clathrate hydrates at too high a temperature (T > \sim 150 or 200 K) causes the guest molecules to pump away, leaving ice Ih. (However it is possible to maintain clathrate hydrates under vacuum at low temperatures for a long time without loss of guest molecules. For example, in air thermal conductivity experiments we maintained an sample at T \sim 100 K for some months without measurable loss of guest molecules). It does not appear possible to stabilize the empty host lattice by this method, nor by any other method yet known. However if one was able to find a way to produce the empty lattice this would be a very important contribution to this field, as it would allow further experiments which would answer many outstanding questions about the unusual properties of clathrate hydrates.

Name of Speaker : E. WHALLEY for SMOLUCHOWSKI

Comment of K. ROESSLER:

There of so many gas phase reaction which build-up organic and inorganic molecules, that a conclusion from the composition of the coma for the presence of the molecules in form of clathrate in the nucleus is not possible.