7.1 ICE NUCLEATION

Water is one of the basic commodities on which our civilization depends and it is no accident that the highly developed or advanced regions of the world are those which are endowed with good supplies of water. Practically the whole of our usable water comes in the form of precipitation from the atmosphere [28]. A complete understanding of how water is stored in the atmosphere and how it precipitates out, still eludes atmospheric scientists.

In the atmosphere, precipitation from clouds depends upon the ability of water molecules to coagulate and grow into rain drops large enough to fall, or get adsorbed to form ice crystals, at the expense of neighbouring water droplets, which finally become big enough to fall down under gravity as snow crystals or, if they melt, as rain drops. In both cases nucleation of a critical sized embryo becomes essential. The nucleation in the atmosphere is generally heterogeneous and the water vapour pressure in the atmosphere never reaches the value required for homogeneous nucleation to take place.
Nucleation of ice and growth of ice crystals have fascinated many research workers for a long time. Studies on nucleation of ice have served as models for nucleation and growth of crystals in general. The variety of growth forms exhibited by snow crystals grown from vapour has attracted the attention of many scientists and has prompted them to come out with possible theories of growth of crystals.

The widespread use of silver iodide as seeding nuclei in clouds has opened up not only the possibility of artificial rain-making, but also the possibility of suppression of excess rainfall or hailstorms. The efficiency of silver iodide particles as catalysts for ice nucleation has led to detailed study of the nature and properties of silver iodide which make it so.

The most striking property of silver iodide which reveals itself immediately is its lattice structure which resembles that of an ice crystal. It has however been shown that though lattice match may be an important criterion for heterogeneous nucleation of ice, it is not the only requirement. On the other hand, it has been shown that substances without any lattice similarity also nucleate ice, in some cases the efficiency being better than some substances with lattice similarity. What perhaps is equally
important, is the adsorption property of the substrate surface.

Several attempts have been made to find the dependence of ice crystal shape upon the variables involved in the growth process. Parameters which almost certainly affect crystal habit are the temperature and the ambient pressure of water vapour. It is also possible that foreign particles or vapour may exert appreciable influence on the growing ice crystal [28].

7.2 SUMMARY OF PRESENT STUDY AND CONCLUSIONS

In this study, Chapter 1 gives a general introduction about nucleation and growth habits of ice crystals with particular reference to heterogeneous nucleation of ice on substances like silver iodide and complex substances containing silver iodide. The properties required for a good ice-nucleating material are discussed in the light of experiments done with silver iodide as catalyst. Results of ice nucleation studies with materials having silver iodide as one of the components have been summarised especially in the case of nucleating particles, suspended in water. A review of the work concerning ice crystal habit change is also given. Finally the probability of formation of quasi-liquid layer on ice just below the melting point is discussed.
Size of the nucleating particle is an important parameter in heterogeneous nucleation of ice. Nucleation efficiency generally increases with the size of the particle. In Chapter 2, nucleation efficiency has been obtained as a function of particle size in the case of condensation, sublimation and freezing of water assuming a cylindrical embryo growing symmetrically on the prismatic edges of a hexagonal or cubic prism. The results obtained especially for supercoolings show better agreement with values expected for heterogeneous nucleation of ice. It also shows that the growth of ice crystals along the edges of hexagonal prism substrates is a definite possibility.

Another important requirement for a good ice nucleating agent is that it should have sufficient number of surface active sites at which the embryo starts to grow. In Chapter 3, the role of such active sites on the substrate particles in ice nucleation is discussed. The expression for nucleation rate for a particle suspended in water is modified incorporating the number of available active sites on the surface of suspended particle. Taking the number of foreign atoms on the substrate surface as the probable number of active sites, the energy for self diffusion of water molecule across water-ice interface is obtained taking into calculation the experimental values of supercooling obtained for nucleation of ice by particles of AgI-AgBr-CuI.
solid solutions suspended in water. The value of the activation energy thus obtained agrees very well with the suggested values for water molecules. Therefore, one more property of the substrate particle i.e., the number of active sites, is included in the rate expression. Introduction of the number of active sites is certainly justified since the nucleation rate will definitely be influenced by the presence or absence of active sites. The rate should normally increase with increase in the number of active sites.

Lattice match is no doubt an important criterion for heterogeneous nucleation of ice. In the case of epitaxial growth, whenever there is a small lattice mismatch or disregistry between the substrate and the growing embryo, the mismatch will be partly taken up by strain energy and partly by a grid of dislocations at the interface between the substrate and the embryo. In Chapter 4, the values of supercooling $\Delta T$ required for formation of ice, have been calculated for different values of disregistry in the case of freezing of water by suspended particles. These values have been calculated assuming the disregistry between ice and pure silver iodide and the supercooling required for formation of ice on pure silver iodide. The variation in lattice spacings and hence the variation in disregistry due to formation of ternary and binary solid solutions of AgI
with AgBr and CuI or AgI with AgCl have been experimentally measured. The supercoolings for different compositions of the above materials have also been measured. The experimental values obtained agree very well with the values of supercoolings calculated in the case of freezing of water by suspended particles.

The values of supercoolings have been calculated assuming the shape of the growing embryo to be a spherical cap on a plane substrate and a cylinder on a plane substrate. The values calculated on the basis of a spherical cap geometry is found to agree better with the experimental values than the values obtained using the embryo geometry of a cylinder on a plane substrate.

The interfacial free energy between growing ice embryo and the substrate is likely to depend on various parameters like supercooling, polarizability, nature of the substrate surface etc. This, in turn, will affect the growth rate and the size of the critical embryo. In Chapter 5, assuming a modified expression for nucleation rate as in Chapter 3, the dependence of the interfacial energy and the shape factor on the number of foreign atoms on the surface of AgI substrate has been discussed in the light of experimental results obtained in the case of ice nucleation by suspended particles of AgI-AgBr-CuI solid solutions. It has been shown that the nature of the pure substrate surface
has been altered due to the presence of foreign atoms which result in change in the value of interfacial energy which in turn affects the supercooling required for ice nucleation.

Chapter 6 deals with the growth habit of ice crystals. A quasi-liquid layer is known to exist over the ice surface temperatures just below 0°C. Taking into account the existence of quasi-liquid layer up to a certain temperature below 0°C and assuming that the tip of a growing dendrite has the shape of a paraboloid of revolution, an expression is obtained for the mean migration distance of a water molecule on the basal plane of the ice crystal in terms of the supercooling. A similar variation in mean migration distance over the prism face of the ice crystal, if suitably assumed, can be used to explain the variation of ice crystal habit with temperature. When more molecules aggregate on the prism face than on the basal face a plate-like growth occurs. Similarly, when more molecules aggregate on the basal face than on the prism face a column like or dendritic growth occurs.

7.3 SUGGESTIONS FOR FURTHER WORK

As mentioned in Chapter 1 ice nucleation problem is an enormous one involving crystallographical, physical, chemical, dynamical, thermodynamical, and statistical implications. In this study, some aspects of nucleation and growth of ice crystals like the shape of the embryo,
heterogeneous nucleation on substrate particles, effect of size, surface active sites, the role of foreign atoms on the surface of the substrate particles, the strain energy due to misfit and its effect on nucleation of ice embryo, the activation energy of water molecules, nucleation rate and growth mechanism of ice crystals, have been looked into from a different angle on the basis of the experimental evidences wherever available.

However, it is unlikely that any study undertaken is either complete or comprehensive covering all aspects of ice nucleation. Considering the amount of laboratory and field work done in this area, it is nearly impossible to cover all the aspects and explain all the experimental observations. The important difference between laboratory observations and field tests lies in the fact that certain quantities like temperature and supersaturation which can be sufficiently controlled in the laboratory tests, could not be controlled when field tests are conducted in the atmosphere. All the investigation methods used in ice nucleation are still inaccurate and often very discontinuous. The data obtained are fragmentary. However we must accept studies of cases, for isolated and limited phenomena, as well measured as possible, that is, for which all measured parameters have been controlled with best accuracy [2].
This study has been mostly confined to heterogeneous nucleation of ice by particles suspended in bulk water and a few aspects of vapour growth of ice crystals. The complete understanding of nucleation of water and ice is necessary if the study is to be extended to nucleation in the atmosphere. Further, whatever may be the results obtained in laboratory experiments, corresponding measurements must be made in the atmosphere. This presents a lot of problems like dispersal of aerosol, controlling the size of the aerosol, counting the number of ice crystals or rain drops formed and thermodynamic conditions governing the action of nuclei etc.

The expression for nucleation rate of ice crystals should be suitably modified to incorporate all factors including the nature of the substrate particles, like adsorption sites, lattice match, polarizability, size and shape of the particles. More insight into the growth habit of ice crystals may provide useful information for analysing the results obtained by experiments on ice nuclei.

One more factor which most certainly affects nucleation phenomena is the interfacial energy between the growing embryo and the substrate. It is well known that there could be no justification for using the macroscopic values of the interfacial energy for an embryo consisting of only a few molecules. Also the variation in the interfacial energy is brought about by the nature of the surface, the
strain undergone by the embryo and sometimes the substrate, and the amount of dislocations produced, apart from the major factors of temperature and supersaturation. This aspect of the nucleation problem needs a thorough investigation probably in terms of molecular model.

Another major factor to be taken into consideration is the decay of the activity by nucleating materials due to ultraviolet light or aging. How these factors affect or influence the activity is not still clearly understood. Also the effect of soluble salts present in the atmosphere on nucleation of water and ice should be thoroughly understood for any useful prediction about formation of rain drops or ice crytals to be made.

Almost the whole of this study is devoted to heterogeneous nucleation of ice on substrates like silver iodide. This is so because, the ability of silver iodide as a seeding material in clouds has been well established. For using other materials or solid solutions containing silver iodide in cloud-seeding experiments, necessary pyrotechniques have to be developed for dispersal of such materials in required size in the atmosphere. Field tests involving these materials will also have to be done to make any correlation between laboratory results and measurements in the atmosphere.
Finally, it seems relevant and appropriate to sum up the suggestion in the words of Fletcher [164]:

'It does not seem unreasonable to suggest that a proper understanding of nucleation phenomena will come not so much from continued nucleation experiments or refinements in macroscopic theory of nucleation ... but rather from further fundamental studies on the structure and energetics of the interface involved and the adsorption and growth phenomena associated with same'.