3.1 INTRODUCTION

In the case of heterogeneous nucleation of ice, the nucleation capability of a particle depends significantly on many factors like a) lattice match and crystallographic symmetry, b) water solubility, c) size of the particle, d) polarizability, e) hydrophobicity and hydrophilicity, f) surface charge and g) number and strength of surface sites capable of adsorbing water molecules [4,17,26,126,131-139]. These adsorption sites include sites provided by foreign atoms or ions, behaving like hydrophilic centres on a relatively hydrophobic surface [135]. Zettlemoyer et al [140] found that hydrophobing a silica surface significantly enhanced its ice nucleating efficiency and that some types of these silica materials were as effective as AgI in nucleating ice. Studies of adsorption properties of these types of silicas revealed that water was adsorbed in clusters on high energy sites. Infrared measurements on various types of silicas showed that a balance between hydrophilic and hydrophobic surface groups, together with a proper distribution of sites, is important for the heterogeneous nucleation of ice [141].
Silver iodide, having a low water solubility and a crystal lattice closely resembling that of ice, has an unexpectedly poor ice nucleating ability when highly purified, compared to silver iodide containing impurity ions [116, 136].

Ice nucleation is a very localized phenomenon in that it takes place at distinct active sites which are capable of initiating such nucleation. These are generally active with respect to both water vapour adsorption and water nucleation [4]. The pure material possesses a large number of such sites and relatively inactive physical adsorption sites at its surface [135, 137]. In the case of a water insoluble particle, when it becomes submerged in water, it is surrounded by a large number of water molecules. If the surface of the submerged solid particle is generally hydrophobic, but contains hydrophilic sites, water molecules are preferentially adsorbed at these sites [4]. In this case also such hydrophilic sites may be provided by foreign atoms or ions on the surface of the immersed particle.

The remarkable performance of silver iodide as an ice nucleating agent, nevertheless has something to do with its lattice structure [9]. Lattice matching influences the surface energy which is the energy per unit area at the ice-substrate interface. The surface free energy is
actually lowered when there is matching. This lowering of energy per molecule depends on the potential shape and misfit, but total energy lowering per unit area depends also on the number and density of matching sites [1].

Attempts have been made to reduce the misfit between silver iodide and ice by preparing solid solutions of silver bromide or copper iodide or both with silver iodide [19, 26, 54]. Varying the percentage of silver bromide or copper iodide added to silver iodide to form a solid solution, the misfit between the solid solution and ice was varied. A study of ice nucleation activity of such solid solutions has revealed an increase in the nucleation activity for a decrease in the misfit. But still no unique correlation has been established between ice nucleation threshold and crystallographic symmetry or misfit. The main reason for this irregular behaviour is the role played by active sites.

3.2 ACTIVE SITES

As already mentioned, foreign ions or atoms on the surface of a nucleating agent, may provide hydrophilic centres on a relatively hydrophobic surface and water molecules are preferentially adsorbed at these sites. In this Chapter, the expression for nucleation rate by a particle suspended in water is modified incorporating the number of active sites which are capable of nucleating ice. The increase in the number of active sites should increase
the nucleation rate also. As far as the present study is concerned the increase in the number of such active sites is taken to be brought about by the increase in the number of relatively hydrophilic centres due to the presence of foreign atoms on an otherwise relatively pure silver iodide surface which is hydrophobic.

However each one of the foreign atoms on the surface may not give rise to one embryo at a particular supercooling due to sintering of such active sites or due to 'screening zones' formed around the growing embryo in which no nucleation occurs practically [133, 138].

The critical free energy for nucleation of ice is estimated for different amounts of bromine or copper atoms on the surface of silver iodide particle in the case of AgI-AgBr-CuI solid solution. The misfit strain energy also is taken into account in arriving at this estimate. From this energy required for self-diffusion of a water molecule is calculated.

3.3 ACTIVATION ENERGY

In order to apply the nucleation rate equation to the case of ice formation in supercooled water, it must be realised that the main difference between nucleation of ice embryos from supersaturated vapour and supercooled water lies in the growth mechanism of embryos. In the former case
growth of an embryo is controlled by monomer flux from the water vapour. In the latter case, where water molecules are already in contact with the ice embryo, growth is a matter of molecular re-orientation involving the breaking of 'water-to-water' bonds and formation of 'water-to-ice' bonds. In this process, a water molecule must pass from its average equilibrium position of minimum potential energy in water to a new equilibrium position in ice, the two positions being separated by an energy barrier $\Delta g$. $\Delta g$ can be expressed as the energy of activation for diffusion across the ice-water interface. It can also be termed as activation energy for self-diffusion.

3.4 NUCLEATION RATE

When a particle is suspended in water, the rate at which it nucleates can be written as

$$J = \frac{kT}{h} n_c 4\pi r^2 \exp\left(-\frac{\Delta g}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$

(3.1)

where $k$ is the Boltzmann's constant, $h$ the Planck's constant, $T$ the nucleation temperature, $r$ the radius of the nucleating particle suspended in water and $n_c$ the number of water molecules in contact with unit area of the surface of the particle. $\Delta g$ is the activation energy for self-diffusion in liquid or more precisely across the liquid-solid boundary [3,28]. $\Delta G^*$, the critical free energy for
the formation of nucleus, depends on the interfacial free energies and the shape of the growing embryo. The pre-exponential term in Equation (3.1) takes care of the size of the nucleating particle, the number of water molecules on the surface and the frequency per unit area with which the molecule of the right type jumps into the surface of the cluster.

However this expression does not reveal any dependence of the critical free energy on the nature of the surface of the suspended particle, particularly the availability of active sites capable of adsorbing water molecules. In other words the expression does not make any distinction between a substrate particle whose surface is devoid of preferential nucleating sites and that which contains a large number of such sites.

The nucleation rate is normally expected to increase as the number of active sites available increases. Hence, it is proposed that a correction term should be included in the expression for nucleation rate. Assuming that the rate increases proportionately with the increase in the number of active sites, the expression given by Equation (3.1) is modified as,

\[ J' = \frac{kT}{h} \left( -4\pi r^2 n_c \right) n' \exp \left( -\frac{\Delta g}{kT} \right) \exp \left( -\frac{\Delta G^*}{kT} \right) \]

(3.2)
where \( n' \) will be the number of sites which nucleate corresponding to a critical free energy of \( \Delta G^* \) for a particular nucleation temperature \( T \).

\( n' \) will depend on the total number of active sites available on the surface of the immersed particle. All the sites available will not be active at a particular temperature \( T \). More and more sites will become active as temperature decreases i.e., supercooling increases. As already mentioned in Section 3.2, foreign atoms or ions on the surface of the suspended or immersed particle may serve as hydrophilic starting centres for the onset of nucleation.

If \( n_o \) is the available number of foreign atoms on the surface of the suspended particle, then it can be assumed that there will be a maximum of \( n_o \) hydrophilic starting centres available for ice nucleation. But only \( n' \) among these will be the number of sites where the free energy change for the formation of an embryo reaches a critical value \( \Delta G^* \) for the given supercooling. Then we can write using Boltzmann distribution,

\[
n' = n_o \exp \left( -\frac{\Delta G^*}{kT} \right) \tag{3.3}
\]

It should be remembered here that the exponential term in Equation (3.3) already appears in Equation (3.2) and hence Equation (3.2) is modified as,
Equation (3.4) can now be used to determine the activation energy for self-diffusion.

3.4.1 Evaluation of $n_C$ and $n_Q$

The number of water molecules in contact with unit area of the suspended substrate particle, will be the same as the number of water molecules per unit area on the surface of bulk water. Assuming the density of water, the volume of 1 molecule of water is calculated. Assuming each molecule to be spherical, the average radius and hence the number of molecules which will occupy unit area can be found. Adopting this procedure the value of $n_C$ is found to be about $6.7 \times 10^{14}$ cm$^{-2}$.

A similar procedure is adopted for calculating the number of AgI molecules per unit area. This number is calculated to be $3.88 \times 10^{14}$ cm$^{-2}$. This means we are considering the surface which has both Ag$^+$ and I$^-$ ions in equal numbers. The number may be different if only Ag$^+$ or only I$^-$ ions are present in a particular surface presented. However, we will confine our attention to only surfaces having zero net charge, since nucleation occurs more readily on such surfaces [49]. Having determined the number of AgI molecules on the surface of the particle, the number $n_Q$ of
foreign atoms or ions on unit area of say AgI-CuI-AgBr solid solution will simply be $3.88 \times 10^{14} \times \text{(fraction of foreign atoms or ions)} \text{ cm}^{-2}$.

### 3.4.2 Calculation of $\Delta G^*$

Knowing the value of $n_0$, $\Delta G^*$ can be evaluated for each value of $n_0$ from Equation (3.3) provided $n'$ is known. In all the experiments conducted with immersion nuclei, the threshold temperature is determined when at least one embryo attains and crosses the critical size. This means that at least one site out of the available $n_0$ sites, nucleates with the critical free energy of the embryo being $\Delta G^*$.

When $n' = 1$ from Equation (3.3)

$$\frac{\Delta G^*}{kT} = \ln n_0$$

(3.5)

and hence $\Delta G^*$ can be estimated for different values of $n_0$ which in turn means, for different values of fraction of foreign atoms.

### 3.5 ENERGY FOR SELF-DIFFUSION

As mentioned in section 1.4.3, the ice nucleation behaviour of AgI-AgBr-CuI particles have been studied for various percentage compositions of AgBr and CuI and the nucleation temperature determined in each case [26]. Hence using Equation (3.2), $\Delta g$ can be calculated for each value of
the composition of foreign atoms on the surface of the AgI-AgBr-CuI particle, since $\Delta T$ and hence $T$ for each composition is known from Figure 1.1, the numerical values of which are reproduced in Table 3.1. Thus the energy for self-diffusion can be calculated for the different samples and the results are shown in Figure 3.1.

3.6 DISCUSSION

The energy required for self-diffusion of a water molecule across ice-water interface is estimated using Equation (3.2) which incorporates a factor related to the number of active sites. The order of magnitude of $\Delta g$ is reasonable and remarkably close to that suggested by Fletcher [28] indicating the validity of assumptions made. It is found to decrease uniformly as the percentage of foreign atoms on the surface is increased as can be seen from Figure 3.1. However, no bearing on supercooling is evident though the range of supercooling taken for consideration is very limited.

It also shows that the modified rate expression as given by Equation (3.4) is reasonable in that it also incorporates one more factor, i.e., the number of active sites, in addition to several other factors which affect the nucleation rate. One more property of the substrate particle in the case of heterogeneous ice nucleation has
Table 3.1 Experimental values of supercooling for different compositions

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Percentage of composition</th>
<th>AgI</th>
<th>AgBr</th>
<th>CuI</th>
<th>$\Delta T$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95</td>
<td>2.5</td>
<td>2.5</td>
<td>2.221</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>2.15</td>
<td></td>
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<tr>
<td>3</td>
<td>85</td>
<td>7.5</td>
<td>7.5</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>10</td>
<td>10</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>12.5</td>
<td>12.5</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>70</td>
<td>15</td>
<td>15</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>65</td>
<td>17.5</td>
<td>17.5</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>20</td>
<td>20</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>55</td>
<td>22.5</td>
<td>22.5</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>0.48</td>
<td></td>
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<tr>
<td>11</td>
<td>45</td>
<td>27.5</td>
<td>27.5</td>
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<td></td>
</tr>
<tr>
<td>12</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>35</td>
<td>32.5</td>
<td>32.5</td>
<td>0.78</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3.1 Activation energy of a water molecule.
been incorporated in the rate expression. The fact that a reasonable value for the activation energy for self-diffusion is obtained shows that the inclusion of the correction term for the number of active sites is justified.