CHAPTER ONE
INTRODUCTION

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CHAPTER – ONE

INTRODUCTION

Water exists in three phases in atmosphere that is vapour, liquid and solid. The phase change of water plays an important role in cloud microphysics. When water vapour condenses into liquid water droplets or snow crystal, the first stage to it, is the formation of embryo. This phenomenon is called nucleation.

The embryo is the aggregation of a number of water molecules. The embryos smaller than a critical size evaporate while those of bigger size grow further to form water droplets or ice crystals. The initiation of liquid water (or ice) from condensation (or deposition) of water vapour is known as nucleation. The formation of new phase by the expansion of metastable original "mother phase" takes place spontaneously as a result of temperature and density fluctuation in the original phase, provided supersaturation exceeds the critical value.

1.1 SURFACE PROPERTIES OF WATER SUBSTANCE:

SURFACE TENSION: Phases in contact are separated by a thin transitional region, a useful abstracting is to regard such as interface as a geometrical surface. To include surface effect, in complete analogy to the contribution -PdV of pressure volume work the internal energy contribution is given by $\sigma \, dS$, where $S$ is the area of the surface of separation and $\sigma$ the surface
tension. The quantity $\sigma$ is an intensive thermodynamics variable and has dimension of energy per unit area or force per unit length.

**1.1.1 EFFECT OF TEMPERATURE ON SURFACE TENSION:**

Due to thermal agitation, the surface tension of water decreases with increasing temperature. This behaviour has been investigated experimentally by Dorsch and Hocker [1]. For the interval 0 to 40°C the data can be reproduce to within ±0.02 dyne cm$^{-1}$ by the following expression

$$\sigma_{W/a} = 76.10 - 0.155T$$

(1.1)

when $\sigma_{W/a}$ is in dyne cm$^{-1}$ or erg cm$^{-1}$, and $T$ is in °C. From Fig. 1.1, equation (1.1) represents a reasonable extrapolation for the temperature interval 0 to -40°C.

**1.1.2 RADIUS DEPENDENCE OF SURFACE TENSION:**

Due to attractive forces between molecules near the surface, surface tension arises. Hence we may expect that only and attraction of average geometrical configuration of these molecules on a size scale comparable to the effective range of the attractive forces would significantly affect the surface tension. Thus we expect a dependence of $\sigma_{W/a}$ on size only for extremely small drops, consistency of nearly a few tens or hundred of water molecules. The surface tension of water decreases with decreasing radius of curvature of water surface. Tolman [2-3] estimated that $\sigma_{W/a}$ for a drop, which consists of 13 molecules of water, equivalent to a drop radius of $4.6 \times 10^{-8}$ cm, based on $v_o =$
Figure 1.1 Variation of Surface tension of water (against air) with temperature.
30 \times 10^{-24} \text{ cm}^3 \text{ and } \rho_0 = 1.0 \text{ gm cm}^{-3} \text{ is } 40\% \text{ smaller than that for a plane water surface. Benson and Shuttleworth [4] computed this surface tension of a small group of water molecules by counting the number of bonds, which had to be broken in order to cut off the group of molecules from the bulk water structure. In order to estimate the interaction energy between water molecules in water it was assumed that only the first and second nearest neighbour has to be considered. In this manner they predict that the surface tension of a drop of 13 molecules is only 15\% Smaller than that for a plane water surface.}

Following Defay \textit{et. al.} [5] a simple, approximately quasi thermodynamic derivation of a radius dependence of \( \sigma \) is given by

\[
\sigma_{m/v} = \frac{(\sigma_{m/v})_\infty}{1 + (2/a)[\Gamma_{\infty}(m/v)/(\rho_0 - \rho_v)]}
\]  

(1.2)

Where \( \sigma_{m/v} \) is the surface tension of a plane water surface, \( \Gamma_{\infty}(m/v) \) the absorption and the term \( \Gamma_{\infty}(m/v)/(\rho_0 - \rho_v) \) is dependent of radius ‘a’

Table [1.1] shows results of \( \sigma_{m/v}(a) \) computed from equation (1.2). Using \( \Gamma_{\infty}(m/v) \approx 0.87 \times 10^{-6} \text{ mol cm}^{-2} \text{ and approximation } \rho_v < < \rho_0 = 1 \text{ gm cm}^{-3} \). It is seen that the radius dependence becomes important for \( a < < 10^{-6} \text{ cm} \).

\textbf{1.1.3 SURFACE TENSION AT WATER – VAPOUR INTERFACE:}

The difference between the pressure \( \rho_0 \) inside a water drop of radius ‘a’ and the pressure \( \rho_v \) of vapour with which it is in equilibrium is given by

\[ \text{...} \]
\[ \rho_o - \rho_v = \frac{2\sigma_{o/v}}{\alpha} \]  \hspace{1cm} (1.3)

where we introduce \( \omega/\alpha \) for the surface tension to emphasize that it is the water vapour interface which is involved. Given that \( \sigma_{\omega/v} \approx 76\text{dyne cm}^{-1} \) at 0°C, we see that the pressure difference is about 1.5 atm for \( a = 1 \) at m smaller drops have corresponding larger internal pressures.

For practical purposes, we can replace \( \sigma_{\omega/v} \) by \( \sigma_{\omega/a} \), the surface tension for a water humid air interface. Experimentally, \( \sigma_{\omega/a} \) increases by less than 0.05% if air at 1 atmosphere is replaced by pure water vapour at saturation pressure (at the same temperature).

**1.1.4 SURFACE TENSION AT ICE VAPOUR INTERFACE:**

Surface energy of ice is the energy required to form an unit area of low surface. For ideal crystalline ice this energy may be identified with one and a half the energy per unit area, \( W_c \), which is needed to split an infinite crystal parallel to a particular crystallographic plane and separate the two parts by an infinite distance. It is natural to take \( W_c/2 \) as the surface tension or interfacial energy \( 64/\alpha \), between the particular ice crystal face and water vapour, assuming the presence of such gases does not affect the surface energy.

Disregarding the forces of interaction due to third or higher order nearest neighbours, energy per molecule required for cleavage of an ice crystal can be expressed as

\[ E_m = U_1 + 6U_2 \]  \hspace{1cm} (1.4)
Where $U_1$ and $U_2$ are the average interaction potential between the molecules in the first and second interaction zones. The interaction potentials $U_1$ and $U_2$ for intermolecular spacings of $2.76 \times 10^{-8} \text{ cm}$ and $4.51 \times 10^{-8} \text{ cm}$, respectively, were computed on the basis of force constants, which take account of the multiple electrostatic interaction forces, induction forces, and repulsive forces. As a result, Reuck [6] found $NaEm = 6.08 \text{ kcal mol}^{-1}$, or $Em = 4.22 \times 10^{-13} \text{ erg per molecule}$, for an ice crystal in vacuum at 0°F.

The estimated values of $We$ for different shapes of ice crystals are $We(B) = 238 \text{ erg cm}^{-2}$ for the Basal faces of ice and $We(p) = 253 \text{ erg cm}^{-2}$ for the prism faces; the corresponding values for the surface energies are $\sigma_{iv}(B) = 119 \text{ erg cm}^{-2}$ and $\sigma_{iv}(p) = 126 \text{ erg cm}^{-2}$. Similar estimates were made by McDonald [7].

**1.1.5 SURFACE TENSION AT ICE WATER INTERFACE:**

Consider a system surrounding by super cooled water, consisting of ice crystals. The surface tension between ice and super cooled water $\sigma_{i/w}$ must be considerably less than $\sigma_{iv}$ because the forces between water molecules and the spatial arrangement of molecules in super cooled water are not too different from those in ice is very difficult to determine $\sigma_{i/w}$ by experimental techniques, and the results of numerous attempts show considerable spread Fig. 1.2.
Comparison of results from semi empirical methods and experiments reveals an overall consistency. A reasonable relation for the variation of $\sigma_{i/w}$ with the temperature is given by

$$\sigma_{i/w} = 28.5 + 0.25 T$$  \hspace{1cm} (1.5)$$

where $\sigma$ is in erg cm$^{-1}$ and $T$ is in °C. This relation does not discriminate between the Prism and Basal plane of the ice lattice. As with ice crystals growing from the vapour, ice crystals growing from super cooled water do not have a molecularly smooth surface. Direct photographic evidence of the presence of steps at a growing ice water interface has been provided [8-9].

Some of the observed steps had spiral forms appearing at a number concentration of about $10^2$ cm$^{-2}$, with step heights between 0.1 and 4 µm and spacing between the steps of 5 to 20 µm. These observed step heights are enormous considering that they probably originated on screw dislocations. No explanation for this observation is currently available except to say that, as in the case of step formation at the ice air interface some sort of bunching mechanism may be operating.

1.2 CHEMICAL POTENTIAL:

When the phase change takes place there is a certain amount of energy, in the form of latent heat, is given out or observed. This energy is called the chemical potential energy.

1.2.1 CHEMICAL POTENTIAL OF WATER VAPOUR IN HUMID AIR:
Through the equilibrium, we derive Chemical potential of water vapour and water in aqueous solution. We have equation,

\[
\left( \frac{\partial \mu_k}{\partial T} \right)_{P,n_i=x_k} = -\left( \frac{\partial S}{\partial n_k} \right)_{T,P,n_i=x_k} = S_k
\]  

(1.6)

From equation (1.6), we have for an ideal gas K

\[
\left( \frac{\partial \mu_k}{\partial T} \right)_{P,n_i=x_k} = V_k = \frac{RT}{P_k}
\]  

(1.7)

After integration

\[
\mu_k = \mu_{k,0} + RT \ln P_k
\]  

(1.8)

In above, the integration constant uks depends only on the temperature. The potential pressure for such a mixture is \( P_k = X_k P \). Thus we can write equation (1.8) as

\[
\mu_k = \mu_{k,0} + RT \ln P + RT \ln X_k
\]  

(1.9)

Therefore if we assume pure water vapour at pressure \( e \) is an ideal gas, its chemical potential is

\[
\mu_{v,0} (e, T) = \mu_{v,0}^* (T) + RT \ln e
\]  

(1.10)

Where \( \mu_{v,0}^* (T) \) is the chemical potential at a standard state of unit pressure. Similarly the chemical potential \( \mu_o (P,T) \) of water vapour in humid air at total pressure \( P \) is

\[
\mu_v (\rho, T, X_v) = \mu_{v,0}^* (T) RT \ln \rho + RT \ln X_v
\]  

(1.11)

From eq. (1.10) with \( e = \rho \), eqn. (1.11) may also be expressed as

\[
\mu_v (\rho, T, X_v) = \mu_{v,0} (\rho, T) + RT \ln X_v
\]  

(1.12)
This shows that $\mu_v = \mu_{v,o}$, since $X_v \leq 1$ unlike pure gases whose chemical potentials vary logarithmically with pressure, the chemical potential of a pure liquid is proportional to pressure to an excellent approximation. It is clear from

$$\left( \frac{\partial \mu_k}{\partial P} \right)_{T,n,k} = -\left( \frac{\partial V}{\partial n_k} \right)_{T,P,n,k} = V_k \quad (1.13)$$

On realizing that liquid are nearly incompressible. Thus, for water we have

$$\left( \frac{\partial \mu}{\partial \rho} \right)_{o} = V_{a,o} \approx \text{constant} \quad (1.14)$$

from which the chemical potential is found to be

$$\mu_{a,o}(P,T) \approx \mu_{a,o}(O,T) + V_{a,o}P \quad (1.15)$$

From above equation, we came to know that the chemical potential of given gas and liquid will be same in both phases, if they are in equilibrium. As a result, from (1.8) the chemical potential of component $k$ in a liquid solution which is in equilibrium with its vapour at partial pressure $P_k$ is

$$\mu_{k,t} = \mu_{k,o} + RT \ln P_k$$

Along with, experiments show that for so called “ideal” solutions, for which there are no interactions between the solvent and solute molecules, the equilibrium vapour pressure of any component is proportional to its mole fraction in solution (This is known as Raoult’s law). Assuming Raoult’s law, then we have $P_k = X_{k,t} P_{k,o}$, where $X_{k,t}$ is the mole fraction of component $k$ in
the solution, and $P_{k,o}$ is the partial pressure of component $k$ in equilibrium with the pure liquid phase of $k$ at the same temperature. Then as a fraction of $X_{k,t}$, the chemical potential becomes

$$\mu_{k,t} = \mu_{k,t}^0 + RT \ln X_{k,t}$$

(1.17)

Where $\mu_{k,t}^0$ is a function of both temperature and total pressure, but is independent of the composition of the solution.

1.2.2 CHEMICAL POTENTIAL OF WATER IN AQUEOUS SOLUTION:

In clouds, water is generally present in dilute aqueous salt solution. Therefore, $\mu_{k,t} = \mu_{k,t}^0 + RT \ln X_{k,t}$ is especially relevant to us and we may use it to write the chemical potential for water in an ideal aqueous salt solution in the following form

$$\mu_w (P, T, X_w) = \mu_w^+ (P, T) + RT \ln X_w$$

(1.18)

Where $X_w = n_w / (n_w + n_s) = 1 - X_s$, is the mole fraction of water, $n_w$ and $n_s$ are the number of moles of water and salt in the solution respectively. By symmetry one would expect that the chemical potential of the salt component could be expressed in the same way, viz.

$$\mu_s (P, T, X_w) = \mu_s^+ (P, T) + RT \ln X$$

(1.19)

In passing, we may note that for $X_w = 1$, $\mu_w (P, T) = \mu_{w^o}(P, T) = \mu_w^+ (PT)$, the chemical potential of pure water at $P, T$. There is no analogous simple physical interpretation for the quantity $\mu_s^+ (P, T)$.
Experiments confirm equation (1.18) and (1.19) for the most dilute solutions of non-electrolytes. In general real aqueous solutions departs from such ideal behaviour. It is customary to account for non ideal solution through the replacement of the mole fraction $x$ by the activity $a = f x$, where $f$ is called the relational activity coefficient. Thus for real aqueous salt solutions we can write

$$
\mu_n (P,T, a_n) = \mu_{n,0} (P,T) + RT \ln a_n ; \quad a_n = f_n X_n
$$

$$
\mu_s (P,T, a_s) = \mu_{s,0}^+ (P,T) + RT \ln a_s ; \quad a_s = f_s X_s
$$

(1.20) (1.21)

The importance of the activity to us is that it provides a direct measures of the equilibrium water vapour pressure over a real salt solution, or in other words, the generalization of Raoult’s law to real solutions.

1.3 CHANGES IN CHEMICAL POTENTIAL:

For a system change in chemical potential is

$$
d\mu = -(\mu_v - \mu_l)
$$

(1.22)

Where $\mu_v$ and $\mu_l$ are the chemical potentials of the vapour phase and liquid phase respectively $d\mu$ shows the energy of the formation of liquid phase.

1.4 GIBB’S PHASE RULE:

This rule enables us to determine the variance of a system i.e. the number of intensive variables, which may be freely specified without cause the system to depart from equilibrium. To derive the phase rule let us consider the heterogeneous, isolated system. In equilibrium the system is characterized by a common $T$ and $P$ and by a number of mole fractions in the various phases.
Let us denote the mole fraction of the \( k \)th component in the \( j \)th phase by \( X_k^j = \frac{n_k^j}{\sum_k n_k^j} \). Then for a system of \( \phi \) phases and \( c \) components there will be \( \phi c \) intensive variables at equilibrium. However, not all of these are independent. Thus, for every phase we have the simple mass conservation constraints that \( \sum_{k=1}^{c} X_k^j \) for a total of \( \phi \) constraints. In additions, we have the condition

\[
\mu_k' = \mu_k'' = \cdots = \mu_k^{(c)}, \text{ for } k = 1, 2, 3, \ldots, c
\]

on the chemical potentials, which constitute another \( (\phi - 1) \) constraints for every \( k \), for a total of \( (\phi - 1)c \) constraints. Therefore, at equilibrium the total variance or number of thermodynamic degrees of freedom is

\[
w = 2 + \phi c - \phi - c (\phi - 1) = 2 + c - \phi
\]

which is the Gribbs phase rule for the bulk phases.

As a simple application of above equation consider a homogeneous fluid, we have \( \phi = 1, c = 1 \) so \( w = 2 \).

This is consistent with the familiar circumstances that equation of state of which a system provides one connection among three thermodynamic state variables (e.g. \( P, T, \rho \)).

For a mixture of two gases, \( c = 2, \phi = 1 \) and hence \( w = 3 \). For water in equilibrium with a vapour and ice, \( c = 1, \phi = 3 \) and \( w = 0 \), equilibrium is possible only for a single choice of temperature and pressure, which defines
the triple point temperature $T_0$ of this system. If this system is now exposed to the atmosphere, $c=2$ (water substance and air), $\varphi =3$ and so $w =1$

1.5 NUCLEATION:

The formation of critical nuclei of water or ice is called the nucleation phenomenon. Before the critical size the embryos are formed of different sizes. Beyond the critical size the nuclei are changed into drops by further condensation of water vapour. But below the critical size the embryos may be vaporized or dissociated. The formation of a new phase at the expense of a metastable original phase (mother phase) does not begin in a continuous manner, but rather takes place spontaneously as result of temperature and density fluctuations (hetero phase fluctuation ) in the original phase provided that a critical supersaturation is exceeded. This spontaneous process is called nucleation.

The nucleation phenomenon has been divided in two categories

1. Homogeneous nucleation
2. Heterogeneous nucleation

1.5.1 HOMOGENEOUS NUCLEATION OF WATER:

It occurs only when supersaturation ratio is several hundred percentages and it may be assumed that foreign substances are absent. But in actual atmosphere only .01 to 0.10 supersaturation (i.e, 1% to 10%) is present in the clouds, hence homogeneous nucleation is not possible generally.
1.5.2 HETEROGENEOUS NUCLEATION OF WATER:

This type of nucleation is generally responsible for cloud formation. Such nucleation is assisted if suitable solid surfaces are some foreign materials like dust particles, cloud seeding particles and ions are present. The heterogeneous nucleation also takes place when external electric filed is applied to the cloud.

Thus, heterogeneous nucleation is of following types;

(a) Ion induced nucleation

(b) The electric field induced nucleation

(c) Nucleation on certain solid surfaces of different shapes and material.

1.5.3 CLOUD CONDENSATION NUCLEI (CCN):

In the atmosphere the drop formation occurs via heterogeneous nucleation involving aerosol particles (AP). AP which are capable of initiating drop formation at the observed low supersaturations are called CCN.

1.5.4 ICE FORMING NUCLEI (IN):

Generally the glaciation of clouds begin at temperature much too warm for homogeneous freezing of water. For example – on one occasion [10] observed ice crystals in a long lived cumulative cloud whose top was probably never colder than -4°C and which was not seeded with ice particles from clouds at higher altitudes. Such behaviour indicates that some fraction of the local AP also can serve as ice forming nuclei (IN).
1.5.5 NUMBER CONCENTRATION OF CCN:

Twomey and Wojciechowski [11] studied CCN concentration over various parts of the world. The results of these studies are summarized in Fig. 1.3a.b.c. The result shows no systematic latitudinal variation in concentration. The observation also confirms that continental air masses are generally richer in CCN than maritime air masses within a particular air mass at flight level. The variation of median CCN concentration was surprisingly small. At supersaturation between 0.1 and 10% the median concentration of CCN was found to range from a few tens to a few hundreds cm\(^{-3}\) in air over oceans and from a few hundred to a few thousand cm\(^{-3}\) in air over the continents.

From Fig. 1.3 it is indicated that the concentration of CCN (i.e. \(N_{CCN}\)) increases with increasing supersaturation \(S_{v,w}\). This behaviour can be expressed as

\[
N_{CCN} = CS_{v,w}^{k}
\]  

(1.24)

Where \(k\) & \(C\) are constants.

At a given location, the CCN concentration is found to vary with time over several orders of magnitude, depending upon the proximity of sources and on meteorological factors such as wind direction, air mass type, precipitation and decreasing or increasing cloudiness [12,13] Fig. 1.4 shows a typical time variation of CCN concentration [14-15] showed that at a given location, repeatable patterns can be detected in the diurnal variation of the CCN.
Figure 1.3 Median world-wide concentration of CCN as a function of supersaturation required for activation; (a) in air over oceans, (b) in air over continents, (c) all observation [20]
Figure 1.4 Variation with time of the CCN concentration activated at 1% supersaturation during March 29, 1968, in air at observation station (2025m) in Olympic Mts., Washington State [22].
concentration. Thus a noon maximum and late evening maximum were observed consistently during one year observation period at Robertson (N.S.W., Australia).

Generally CCN concentration in maritime and modified maritime air masses which have been over land less than two days rarely exceed 100 cm$^{-3}$ while concentration in excess of $10^3$ cm$^{-3}$ are found in air which have been overland for several days Fig. 1.5.

Table [1.2] describes the comparison between total concentration of aerosol particle, the concentration of cloud condensation nuclei activated at 1%. Supersaturation at various locations in Fig. 1.6 shows that the vertical variation of a CCN concentration activated at 0.7% supersaturation over various locations [16].

1.5.6 EXPERIMENTAL VERIFICATION OF HETEROGENEOUS WATER DROP NUCLEATION:

Once water soluble and mixed AP grows with increasing relative humidity, it is appropriate latest the theory of nucleation of such particles in 2 ways:

1. By experimental determination the equilibrium growth of these particles.

2. By determining the number of particles of given size and composition which, become activated at a given supersaturation.

The agreement with theory is satisfactory as regards the shape of CCN spectral actual concentration of activated drops.
Figure 1.5 Variation of the CCN concentration required for activation at various locations, as function of supersaturation [30].
Figure 1.6 Vertical variation of the CCN concentration activated at 0.7% supersaturation over various locations [25].
Attempt to verify the prediction of after drops nucleation on water insoluble partially wettable substrates have been made [17-18]. These experiments were carried out in diffusion chambers where nucleation was forced to take place on plane substrates for which angle of contact of water had been measured separately. Unfortunately, results derived from the experiments show considerable disagreement, while the critical supersaturation necessary for onset of drop nucleation are sufficiently lower for all wetting angles than those predicted by theory.

The results of experiments carried out [18] are reproduced in Fig. 1.7. It is seen that the measured critical supersaturations as a function of contact angle agree fairly well with those of Koutsky et. al. [19] up to a supersaturation of about 10%, corresponding to a contact angle of about 25°.

1.5.7 ELECTRICAL INHOMOGENETIES OTHER THAN IONS:

The surface of the nucleating substrate consists of sharply defined boundaries between surface regions of different electric field sign, or of locations where the electric field vector in the substrate is oriented parallel to the surfaces. Growth of water cluster around electric inhomogeneties other than ions attract water molecules to the substrate surface through interaction between local electric dipoles in sites substrates and the dipole of a water molecule. Growth of the water cluster at such sites can be aided if the diffusivity of water molecules of surface regions with either an inward directed or an outward directed electric field is high as compared to the diffusivity over
Figure 1.7 Critical supersaturation for onset of water nucleation on a plane, water-insoluble, partially wettable substrate, as a function of contact angle of water on substrate. Comparison of experiment with theory [27-28].
the boundary between regions of electrically different sign, or as compared to
the diffusivity over in a area where the electric field vector in the substrate is
oriented parallel to the substrate, since than both the positive and negative ions
of water molecules are partially tied down.

1.5.8 ICE FORMING NUCLEI:

Ice forming nuclei exhibits three basic modes of action

1. In the first mode, water is absorbed directly from vapour phase
onto the surface of IN where at sufficiently low temperatures, absorbed vapour
is transformed into ice.

2. In the second mode, the IN initiate the ice phase from inside in
super - cooled water vapour.

3. In the third mode, in the action, the IN initiates the ice phase at
the moment of contact with the super cooled droplets.

The first mode in the action is called deposition mode and AP which
exhibits this behaviour are called “deposition IN”; the second is called freezing
mode and the corresponding AP are : freezing nuclei”; the third is called
contact mode, participated in by contact angle.

1.5.9 IN CONCENTRATION:

The IN concentration measurements are reproduced as a function
of temperature and location in Fig. 1.8 and 1.9.

Fig. 1.10 shows a day to day variation in IN concentration
observed with one counting technique one particular site. Even at remote
Figure 1.8 Variation of the mean or median number concentration of IN with temperature and geographic location. (1) Bracknell (England), 51° N, 0°W, (2) Clermont-Ferrand (France), 46°N, 3° E, (3) Corvallis (Oregon, U.S.), 44° N, 123° W, (4) Tokyo (Japan), 36°N, 140°E, (5) Tucson (Arizona, U.S.), 32° N, 111°W, (6) Jerusalem (Israel), 32° E, (7) Palmbeach (Florida, U.S.), 27°N, 80° W, (8) Hawaii (U.S.), 20° N, 158° W, (9) Swakopmund (S. Africa), 34° S, 14°E, (10) Sidney (Australia), 34°S, 151° E (11) Tasmania (Australia), 43° S, 147° E, (12) Antarctica, 78° S, 166° E. The dashed line represent $N_{IN} = 10^{-5} \exp(0.6 \Delta T)$. 
Figure 1.9 Range of median number concentration of IN as function of
Temperature for various geographic location; 44 stations.
The dashed line represent $N_{IN} = 10^{35} \exp (0.6\Delta T)$ [38].
Figure 1.10 Variation of the daily number concentration of ice forming nuclei at \(-20^\circ C\) measured during December, 1961, to January, 1962, at Antarctica station. [39].
locations such as Antarctic, pronounced variations in the daily IN concentrations do occur. Similar observation were made [20], who measured at an Antarctic station IN concentration maxima as high as 30 l⁻¹ at 20⁰c. Such high concentration counts were found to last up to two days.

Fig. 1.8 and 1.9 also shows that the IN counts increase nearly experimentally with decreasing temperature Fletcher [21] gave a convenient statement of this behaviour as;

\[ N_{IN} = A \exp(\beta \Delta T) \]  \hspace{1cm} (1.25)

Where \( \beta = 0.6 \ (°C)^{-1}, A = 10^{-5} \ l^{-1} \), where \( N_{IN} \) is the number concentration of IN active at a temperature warmer than \( T \) and where \( \Delta T = T_0 - T \).

Gagin and Huffman [22-24] found that at any given temperature the number concentration of IN increases with increasing relative humidity Fig. 1.11a and correlates logarithmically with the supersaturation over ice independently of temperature Fig. (1.11b) according to the relation

\[ N_{IN} = CS_{\nu - 1}^k \]  \hspace{1cm} (1.26)

Huffman [24] observed that the vertical IN concentration profiles often exhibits a pronounced layer-structure even in the lowest few kilometers above ground. For example a strong concentration maximum was observed during few days of summer time sampling at about 500 meters above ground over St. Louis and over N.E.Colorado. No temperature inversion was present at the time over N.E. Colorado and the inversion over St. Louis was considerably
Figure 1.11 Variation of the IN concentration with (a) relative humidity and with (b) supersaturation over ice.
above the In concentration maximum; thus the concentration maxima appear not to be co-related with the temperature inversion.

### 1.5.10 ENHANCEMENT RATIO OR ENHANCEMENT FACTOR ($R_m$):

The enhancement ratio is defined as a ratio of ice crystal concentration and the IN concentration determined at the cloud top temperature.

The enhancement ratio ($R_m$) can be as large as $10^4$ to $10^5$ at temperatures between -5 and $-15^0\text{C}$. Also $R_m$ tends to decrease with decreasing cloud top temperatures, and reaches unity between $-25$ and $-30^0\text{C}$. Fig. 1.12 represents some observation of $R_m$ over the cascade meters during winters of 1971 to 1973, which are summarized by the best relation:

$$\log R_m = 5.02 + 0.204 T_c$$  \hspace{1cm} (1.27)

where $T_c$ is the cloud top temperature in $^0\text{C}$.

### 1.6. MODELS OF NUCLEATION:

#### 1.6.1. MODELS OF HOMOGENEOUS NUCLEATION:

#### 1.6.1.1. CLASSICAL MODEL:

Within the meta-steady bulk phase of water vapour of small molecular clusters of liquid water, which results from the chons agglomeration of water molecules, these are generally referred to as embryos if the vapour pressure is below the critical value required for nucleation. Such embryos have small binding charges and usually disrupted by thermal agitation. However, at
Figure 1.12 Maximum ice enhancement ratio ($R_m$) in clouds over the Cascade Mts. (Washington State) during winter, 1971-72. (If value is below the detection threshold, it is shown on the threshold line with an arrow attached). As- altostratus, S- stratus, Sc-stratocumulus, Cu-cumulus, C(S)- cumulus with stratified tops [40].
the critical vapour pressure some embryos will reach a critical (germ or nucleus) size, at which point will be unstable equilibrium with the mother phase. A germ will proceed to grow spontaneously and thereby produce a microscopic phase, if a result of fluctuation in the mother phase; its size increases by even an infinitesimal amount. The workers description completely assumed that

1. Pre-nucleation embryos may be regarded water spheres characterized by the usual macroscopic densities and surface tension,
2. they are distributed according to the Boltzmann law.
3. the i-mers are in thermal equilibrium, and the probability that they have the certain energy \( \Delta \phi \), is just the probability for their existence, if we interpret \( \Delta \phi \) as the energy of formation of i-mer.

In this model embryos are considered as spherical of certain radius. The phase change occurs at constant temperatures. The total volume of the system considered (the mother phase + the condensed phase) remains constant.

The Gibbs free energy for formations of spherical i-mer (or embryos) varies in a manner shown in Fig. 1.13. The classical theory provides a simple basis for predicting nucleation rates, which are very similar to those actually observed. The classical amounts of Gibbs free energy \( \Delta G' \) assume embryos are at rest. In the mother phase this energy consists of volume free energy and the surface energy.
Figure 1.13 Energy of i-mer formation as a function of i-mer size, for 0°C.
1.6.1.2 MODIFIED CLASSICAL MODEL:

According [25-26] to the free energy of formation $\Delta G_{i}$, is corrected to new value $\Delta G_{i}'$, which includes the following contributions.

$$\Delta G_{i}' = \Delta G_{i} + G_{i,T} + G_{i,R} - G_{\text{rep}}$$  \hspace{1cm} (1.28)

Where $G_{iT}$ and $G_{iR}$ result from the transational and rotational degree of freedom of embryo. The term $G_{i\text{rep}}$ are called replacement term [25] has been regarded as resulting from the deactivation of the vibrational degrees of freedom which the cluster would have as bulk water.

As the new phase embryos constitute a polymolecular gas in thermal equilibrium with the mother phase, it is apparent that they must have translational and rotational energies, which are overlooked in the classical model. On the other hand the bulk free energy term includes the translational and rotational energy of the bulk water comprising the stationary drop.

Unfortunately, the studies of Lothe an Pound [25-26] and of others suffer from a fairly obvious shortcoming, either the work of formation of germ, or the correction factor itself, or both have to be evaluated for lack of information, in terms of macroscopic values of parameters like $\sigma_{i/w}$ and $\sigma_{w}$. This tends to seriously compromise the macroscopic point of view, which is taken when formulating modification the classical models.

The most feasible way of circumventing such difficulties is the molecular model approach of Plummer and Hole.[27]
1.6.1.3 MOLECULAR MODEL:

This model assumes that certain structures for the embryos i-mers and to determine the corresponding $q_i^{v}$. The size description is available directly. This formulation has the merit of automatically including the terms, which are missing from the classical energy of formation, and of precluding the need for finding “replacement” energy terms. On the other hand one has to be evaluate the partition function $q_i$ Plummer and Hole assumed.

$$q_i = q_{i,T} q_{i,R} q_{i,V} q_{i,R} q_{i,c}$$  \hspace{1cm} (1.29)

Where $q_{i,V} = q_{i,\text{intm}} q_{i,vib} q_{i,\text{inter}}$ is the vibrational partition function given in terms of the intermolecular, intermolecular and vibrational contribution, $q_{i,R} = \exp \left( -\frac{E_{i,R}}{kT} \right)$ is the contribution of the intermolecular binding energy. $E_{i,R}$ to the partition function and $q_{i,c}$ is the configurational contribution to the partition function.

Each of these quantities was evaluated semiempirically in a manner described by Plummer and Hole. In this evaluation it was assumed: 1. That i-mers have a well defined structure, 2. That each structure has a life time sufficiently long to characterize its internal vibrational spectrum, and 3. That the internal structure of a water molecules is negligibly affected by cluster formation.

The assumed structure of water clusters in supersaturated vapour is that of closed or partially closed clathrates composed of five members ring.
Figure 1.14 Cluster models used in the theory of Hale and Plummer. (a) cluster of 20 water molecules arranged in a clathrate structure forming a pentagonal dodecahedron. (b) cluster of 20 water molecules arranged in an ice-I$_b$ structure.
An example of such structures for a 20 mer is shown in fig. 1.14 a. For the study of pre nucleation embryos of ice in vapour [28], assumed and ice in structure composed of rings containing six water molecules each. A typical structure with 20 molecules is shown in fig. 1.14b.

The model calculation for \( q_i \) result in corresponding \( \Delta G_i = \Delta \phi_i \). The values for the case of water embryos are shown in fig. 1.15. The recent approach to the homogeneous nucleation problem uses Monte Carlo techniques to evaluate \( \Delta G_i \). The method is based on a stochastic process, which generates a Boltzmann weighted set of configuration for a given closed system containing a fixed number of molecules.

**1.6.2 MODEL FOR HETEROGENEOUS WATER NUCLEATION:**

The classical model of nucleation theory is used for heterogeneous nucleation. The “replacement term” difficulties associated with the attempt to define the classical approach do not arise, since the nucleating substrate may be taken to be at rest. The modification has been made according to the geometry of surface.

**1.6.2.1 NUCLEATION ON WATER IN SOLUBLE, PARTIALLY WETTABLE CCN:**

It is assumed that water embryos or germ or nucleous nucleated in super saturated vapour on a water insoluble partially wettable surface assumes the shape of a cap.

**1. NUCLEATION ON A PLANARS SUBSTRATE:**
Figure 1.15 Energy of embryo formation versus embryo size (in number of molecules) at $S_{v.w.} = 5.0$ and $T = 273$ K for (i) The classical liquid drop model, $(\Delta F)_i / kT = 9.3 \ i^{2/3} - 1.6 \ i$ (solid line); (ii) The molecular model, $\Delta \phi / kT = 12.8 i^{2/3} - 2.40 i$ (dashed line) [102].
Gibbs free energy for the formation of spherical embryo is given by

\[ \Delta G_{i,s} = \left( \frac{\pi}{3} a_i^3 \Delta G_{\text{vol}} \right) + m_i^2 \sigma_{\alpha/v} (2 + m_{\alpha/v}) (1 - m_{\alpha/v})^2 \]  

(1.30)

Where \( a_i \) is the radius of embryo, \( \sigma_{\alpha/v} \), the surface tension of the water and \( m_{\alpha/v} = \cos \theta \), \( \theta \) being the angle of contact of the surface with water.

2. NUCLEATION ON A CURVED SUBSTRATE:

Fletcher [29-30] has extended the theory to include an amount of the effects of the finite size of the nucleating particle. In this extension the substrate is assumed to be a sphere of radius \( r_N \).

Accordingly, the energy of germ formation becomes

\[ \Delta G_{g,s} = \frac{16\pi M^2_{\alpha} \sigma_{\alpha/v}^3}{3\left[ RT \rho_{\alpha} \ln S_{\alpha,v} \right]^2} f (m_{\alpha/v}, X) \]  

(1.31)

Where

\[ f (m, X) = 1 + \left( \frac{1 - m X}{\phi} \right)^3 + X^2 \left[ 2 - 3 \left( \frac{X - m}{\phi} \right) + \left( \frac{X - m}{\phi} \right)^3 \right] + 3mX^2 \left( \frac{X - m}{\phi} - 1 \right) \]  

(1.32)

With

\[ \phi = (1 - 2mX + X^2)^{1/2}, X = \gamma_N / a_b \]  

(1.33)

Recently [18] modified the heterogeneous nucleation theory of Fletcher to consider nucleation on an insoluble, partially wettable spherically concave substrate of nucleus \( \gamma_N \). The only change in theory is one of geometry.

The volume energy in this case is given by changed value of
Mahata’s computation indicates that concave surface features can be sufficiently enhance the capacity AP to serve as CCN.

**1.7 STRUCTURE OF ISOLATED WATER MOLECULES:**

Measurements of the heat capacity of water vapour at constant volume near room temperature yield a value of approximately 3k per molecule, where k is the Boltzmann constant. Since quantum statistical mechanics shows that the vibrational degrees of freedom are frozen in at these temperature, we must interpret the heat capacity measurement in terms of a contribution of \((1/2)k\) from each of three translational degree of freedom, and a contribution of \((1/2)k\) from rotation about each of the three axes for which the molecule has an appreciable moment of inertia. This interpretation implies that the water molecule cannot have its three atom arranged in the linear fashion. The same conclusion is reached by investigating the electrical properties of the water molecules. Since such measurements reveal a large electric dipole moment of \(\nu = 1.83 \times 10^{18}\) e.s.u. cm\(^{31-32}\) a linear molecule is once again ruled out.

The geometry of the water molecules can be deduced accurately from studies of the infrared spectrum of water vapour. On the basis of such measurements it has been concluded that the three atoms are situated at the...
Figure 1.16 Two dimensional geometry of a single water molecule. The O-H distance (in $10^{-4}$ cm) and the H-O-H angle are indicated, as are radii of the hydrogen and oxygen atoms.
vertices of a triangle the geometry of single water molecule which is given in figure 1.16. Recent experiments show that the equilibrium O-H bond length is 0.95718 Å and that the equilibrium H-O-H bond angle is 104.523° [21].

The structure of the water molecules is importantly affected by the electron configuration around the oxygen atom. In its ground state, an oxygen atom has two electrons in the spherical 1s orbital, where they are bound, in the spherical 2s orbital. In addition, two electrons can be considered to occupy the 2px orbital, one electron the 2py orbital and one electron the 2pz orbital. The electron configuration is illustrated in figure 1.17. Since the 2py and 2pz orbital are incomplete. The electrons in these orbital are therefore free to couple with the electrons in the 1s orbital of the two hydrogen atoms, allowing them to form two O-H bonds.

If these orbitals exactly described the O-H bond of a water molecule, one would expect water to have a bond angle of 90°. Experimentally, however, one finds that the bond angle is some 15° larger. One might try to explain this on the basis of the fact that the O-H in a water molecule is not truely covalent but is partly ionic; i.e. the electrons are not evenly shared by the oxygen atoms and a hydrogen atom, since oxygen is more electronegative than hydrogen, oxygen exerts a greater force on the shared electron pair than does the hydrogen consequently, the electrons spend a greater portion of their time in the outer shells of the oxygen atom than in the hydrogen shells, and so the positive charge of the hydrogen nuclei is incompletely shielded by the
Figure 1.17 Hybridization of orbitals of oxygen atom.
Electrons. Electrostatic repulsion between the two hydrogen atoms must, consequently, lead to an increase of the bond angle.

However, Health and Linnett [33] showed that this repulsion is insufficient to account for the experimentally found bond angle. They suggested that a more significant factor in opening up the bond angle is the mixing or hybridization of the 2s orbital of the oxygen atom with its 2p_y and 2p_z orbital. Two of these overlap with the hydrogen orbital, while the two remaining orbital form two lobes on the side of the oxygen atom away from the hydrogen atoms (Figure 1.17). These lobes, called lone-pair hybrids, are symmetrically located above and below the molecular plane and form roughly tetrahedral angles with the bond hybrids (exact tetrahedral angle 109.467°). It is this tetrahedral character, of water molecule which gives rise to a tetrahedral coordination of water molecules in water and ice.

Duncan and Pople [34] & Bader and Jones [35] have carried out quantum mechanical (molecular orbital theory) calculations of the electron density distribution around a water molecule. Their results confirm the distribution shown in figure 1.17 and show that there are four locations in the water molecules with high electron density; close to the oxygen atom, close to each hydrogen atom and at the location of the lone pair orbital, which appears as an electron density bulge behind the oxygen atom.

The charged distribution around a water molecule may also be approximated by 'electrostatic' or point charge models. In these models points
charges are assigned whose sign, magnitude, and locations are such that the molecule as a whole is electrically neutral, and the electric dipole moment is equal to that experimentally measured. Such models have been worked out [37-40]. Although such models are convenient in some cases, they generally do not predict correctly the higher electric moments [41].

1.8 STRUCTURE OF WATER VAPOUR:

Experiments show that water molecules in water vapour tend to interact and form clusters, in contrast to ideal gas behaviour. Dimers as well as higher order polymers are considered to be present in water vapour, though in small concentration only. Recent experiments involving molecular beam techniques [42-43] suggest that in highly super saturated water vapour, clusters of up to 180 water molecules may be present. Cluster of 21 water molecules seemed to exhibit particularly large stability. It is interesting to note that 21 water molecules can be arranged in the form of a pentagonal dodecahedron with a molecule at each corner and a single molecule in the centre of the ‘cage’.

However, no conclusive evidence of the actual geometric arrangement, if any of water molecules in such clusters in vapour is available at present. Studies on the possible and more likely cluster types have been reviewed [41-44]. Recent theoretical studies of the formation of water clusters have been carried out [45,46,47]. Kistenmacher et. al. found two possible stable configurations for the dimers, a cyclic form and an open form, which
was more stable. For the large clusters the author suggested not a single structure, but a statistical distribution of different configurations, since many configurations with significantly different geometry were found to possess nearly the same energy.

The potential energy of interaction, \( U \) between a pair of water molecules has the general character of being strongly repulsive at very close separations and weakly attractive in longer range. One widely used and relatively simple expression for it is due to Stockmayer [48].

\[
U = -\frac{\mu^2 f}{r^3} - \frac{c}{r^6} + \frac{c\sigma^{18}}{r^{24}} \tag{1.36}
\]

Where \( r \) is the separation of the molecules, \( \mu \) is the dipole moment of an isolated water molecules, \( \sigma \) is the collision diameter (the molecular separation at which \( U = 0 \) if \( \mu = 0 \)), \( c \) is an adjustable constant, and \( f \) is a known function of the mutual orientation of the two molecules.

The first term of the right side of (1.36) is just the dipole – dipole contribution to the interaction energy and may be attractive or repulsive, depending on the dipole orientations. The second term represents contribution from:

(1) The interaction energy between a permanent dipole of one molecule and the dipole it induces in the other (dipole-polarization or induction interaction),

(2) The net energy arising from momentary, fluctuating dipoles interaction with the corresponding induced dipoles (polarization-polarization or
dispersion interaction). Even though the time average of these dipole fluctuations may be zero, the energy contribution is proportional to their mean square, which is finite and positive.

Both (1) and (2) are usually referred to as Wander Waal’s interaction, which by its nature can be seen to bring about an attractive force between the molecules.

The third term in (1.36) represents the short-range repulsive forces, which loosely may be ascribed to the overlap of electronic orbital which are incompatible according to the Pauli Exclusion Principle.

There is little doubt that the Stockmayer potential or similar ones, such as [49-50] potential, portray with fair accuracy the interaction between pairs of water molecules at large separations in dilute water vapour. This is evidenced by the fact that values for the second virial coefficient computed via (1.36) can be made to fit experimental values. On the other hand, the same potential functions yield values for the third virial coefficient of water vapour, which disagree substantially with experiment. Partly, this is due to the approximate nature of (1.36), and partly because three body interactions should be included also, since other molecules in the system can significantly modify the interaction of a given pair. In particular, the stockmayer potential is insufficiently ‘directional’ in character to account for the geometry of cluster formation in water vapour.
1.9 STRUCTURE OF ICE:

Water substance crystallizes from its gaseous its liquid state to form a six-fold-symmetric or hexagonal solid called ice – I_h, at atmospheric pressures and at temperatures between – 100°C and 0°C. At different temperature and pressure ice assumes other crystalline modifications, which are discussed, for example in Fletcher [21] and Hobbs [31]. We shall concern ourselves here only with ice hence forth referred to simply as ice.

X-ray diffraction studies demonstrate that in ice each oxygen atom is surrounded by four nearest neighbour oxygen atoms at a distance of about 2.76 x 10^{-8} cm. These four atoms form an almost regular tetrahedron. In turn, these oxygen tetrahedrons are joined together to form a hexagonal lattice Fig. 1.18. The hexagonal space group is denoted by D_{6h} or P6_3/mmc and is characterized by 1 six-fold axis of rotation perpendicular to 1 mirror-plane, (3+3) mirror planes, and a centre of symmetry.

Near 0°C, any given oxygen atom in ice also has 12 second nearest neighbours at distance of about 4.52 Å, 1 third nearest neighbour at 4.59 Å, 6 fourth nearest neighbours at 5.26 Å, 3 fifth nearest neighbours at 5.31 Å, 6 sixth nearest neighbours at 6.36 Å, 6 seventh nearest neighbours at 6.69 Å, 2 ninth nearest neighbours at 7.36 Å, and 18 tenth nearest neighbours at 7.18 Å.

Each water molecules is hydrogen bonded to its four nearest neighbours. (Generally, a hydrogen bond may be defined as a valence linkage}
joining two electronegative atoms through a hydrogen atom). This is brought about through the formation of two hydrogen (O-H-O) bonds by each water molecule with each bond being directed towards a lone electron pair of a neighbouring water molecule. This manner of bonding leads to an open lattice structure, as illustrated in Figure 1.18. Perpendicular to the \( c \)-axis, the ice lattice consists of open—puckered hexagonal rings (with oxygen atoms alternately raised and lowered). Along the \( c \)-axis are vacant shafts. Comparisons show that the arrangement of oxygen atoms in ice is isomorphous with the Wurtzite structure of ZnS and the tridymite structure of SiO\(_2\).

Each unit cell of ice, a four-sided prism set on a rhombic base, contains four water molecules and is characterized by the lattice constants \( a_0 \) and \( c_0 \) (Fig. 1.19). X-ray data for \( a_0 \) and \( c_0 \) [50-54] are shown in Fig. 1.20 as a function of temperature these measurement shows that \( a_0 \) and \( c_0 \) decrease with decreasing temperature, the rate of decrease is smaller, the lower the temperature—such that \( (c_0/a_0) = 1.629 \) for all temperatures. Using the values for \( a_0 \) and \( c_0 \) given in Figure 1.20, the volume of the unit cell of ice, 

\[
V_{uc} = 2(a_0^2 \sqrt{3/4})C_o , \text{ varies from } 1.305 \times 10^{-22} \text{ (O}\degree \text{C)} \text{ to } 1.281 \times 10^{-22} \text{ cm}^3 (\text{-180}\degree \text{C)}.
\]

Thus, the number of water molecules \( \text{cm}^{-3} \) varies from \( 3.06 \times 10^{22} \text{ (O}\degree \text{C)} \text{ to } 3.12 \times 10^{22} \text{ (180}\degree \text{C)}.

According to Eisenberg and Kauzmann [32], three points of view may be taken to define the hydrogen bond energy \( E_H \) in ice. First, one may assume that \( E_H \) is given by the lattice energy \( E_L \) of one mole of ice (the
Figure 1.18 Position of oxygen atoms in ice-I$_h$: (a) view along c-axis (b) view perpendicular to c-axis.
Figure 1.19 A typical disordered arrangement of protons in the ice-I$_h$ structure; oxygens (1) and (2) contribute 12/12 each, oxygens (3), (4), (5), (6) contribute 1/12 each, oxygens (7) to (12) contribute 2/12 each, and oxygens (13) and (14) contribute 4/12 each, for a total of 48/12 = 4 oxygens [107].
Figure 1.20 Temperature variation of the lattice parameters of ice- $I_h$
difference in energy between one mode of isolated water molecules and one mole of ice, both at 0°K and with motionless atoms), divided by the number of hydrogen bonds in a mole. Since both hydrogen atoms of a water molecule participate in one H-bond (excluding the molecules on the surface of ice), one may estimate $E_H$ as $E_H = E_L / 2 = 7.04 \text{ kcal mol}^{-1}$, based on the value for $E_L$ found by Whalley et. al. [55]. Second one may define $E_H$ possibly more appropriately, in terms of the sublimation enthalpy $(\Delta H)_S$ by writing $E_H = (\Delta H)_S / 2$. Since $(\Delta H)_S$ is temperature dependent, so is $E_H$ and we find $E_H (0^\circ K) = 5.66 \text{ kcal mol}^{-1}$ and $E_H (0^\circ C) = 6.15 \text{ kcal mol}^{-1}$. In both of these definitions we ascribe the entire intermolecular energy in ice to hydrogen bonding. We therefore include in $E_H$ the effect of dispersion and short range repulsive forces which are present not only in ice but also in crystals of non-hydrogen bonded substances. The third definition of $E_H$ is based on the premise that the contribution to $(\Delta H)_S$ from the hydrogen bonds is distinct from that of other forces. One may therefore set $E_H = [(\Delta H)_S - E_{\text{other}}] / 2$, where $E_{\text{other}}$ represents the intermolecular energy associated with the other forces. This definition suffers from the fact that $E_{\text{other}}$ is not as observed quantity, and cannot presently be accurately calculated.

An accurate theoretical calculation of a single hydrogen bond in ice should include at least the effects of nearest neighbours. To date, most investigators have avoided detailed computations for these effects. Generally the approach has been to assume the total hydrogen bond energy is given by
the sum of the four component energies (dipole – dipole, dipole – polarization, polarization – polarizations, and short range interactions), and to evaluate each of these by approximate methods for two neighbouring water molecules at the relative position found in ice. For this purpose, various models for the charge distribution in the water molecule have been assumed. For some component energies, rough estimates for the effect of neighbouring molecules have also been made. The results of the most pertinent calculations on this subject have been summarized [31-32]. The values computed for $E_H$ range from 4 to 8 kcal mol$^{-1}$. In all of these computations, the entire intermolecular energy has been attributed to hydrogen bonding.

The positions of the hydrogen atoms in ice are subject to the Bernal Fowler (BF) rules. These require that (1) each water molecule is oriented such that its two hydrogen atoms are directed approximately towards two or four oxygen atoms which surround it tetrahedrally, (2) there is only one hydrogen atom on each O-D linkage, and (3) each oxygen atom has two nearest neighbouring hydrogen atoms such that the water molecules as a structural unit is preserved.

An ice structure, which obeys the BF rules, is termed ideal. Natural ice, however, does not behave ideally. Numerous experiments imply that a natural ice lattice contains defects, which violates the BF rules. The following major aromatic defects are found in natural ice: stacking faults,
chemical defects, molecular vacancies (Schottky defects), interstitial molecules (Frenkel defects), ionized states and orientational defect (Bjerrum defects).

1.10 ELECTRIC FIELD AND ELECTRIFICATION OF CLOUDS:

Here, we will describe various types of clouds and cloud particle acquire their characteristic state of electrification.

1.10.1 ELECTRICAL STATES OF CLOUDLESS ATMOSPHERE:

Under clear sky conditions, flat portions of the conducting earth carry a negative surface energy density $\sigma_0$ which is approximately $\sigma_0 = -3.4 \times 10^{-4}$ e.s.u. cm$^{-2}$. By Gauss’s law there is a corresponding downward directed surface electric field of magnitude $E_0 = 4\pi \sigma_0$ (e.s.u.) = $3 \times 10^4$ Vm$^{-1}$. The field strength in the atmosphere varies with height in accordance to Coulomb’s law (i.e. as $d^{-2}$) where $d$ denotes distance from the centre of the earth. However, in the rate of attenuation is much lager than this due to the existence of positive space charge, which rapidly screens out the surface field with increasing height.

An approximate empirical description of the variation of the electric field strength with height is.

$$E (\text{Vm}^{-1}) = 81.8e^{-4.52z} + 38.6e^{-0.375z} + 10.27e^{-0.121z} \quad (1.37)$$

Where $z$ is in km. From Gauss’s law

$$\Delta E = \rho/\epsilon_0 \quad (1.38)$$

The corresponding positive space charge density $\rho$ (elementary charges cm$^{-3}$) is
\[ \rho = 20.4e^{-4.52z} + 0.8e^{-0.37z} + 0.069e^{-0.121z} \]  \hspace{1cm} (1.39)

Thus at ground level the charge density is about 21e cm\(^{-3}\), while the average over the first kilometers of the atmosphere is about 5e cm\(^{-3}\).

The small ions produced by cosmic rays and radioactive substances are generally singly charged particles. They may become large ions by attaching themselves too much larger aerosol particles. Since the mobilities of large ions are usually \(10^{-2}\) to \(10^{-4}\) times less than those of small ions, they contribute relatively little to the total ion current. Measurements show that the represented mobilities \(B\) of the small negative ions are greater than the corresponding mobilities \(B_+\) of the positive ions according to Bricard [56], \(B_+ = 1.4 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}\) and \(B_- = 1.9 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}\) at STP.

An extrapolation of these values to elevations \(\leq 10\) km in the standard atmosphere has been computed [57].

\[
\begin{align*}
B_+ &= 1.4 \ e^{0.14z} \\
B_- &= 1.9 \ e^{0.14z}
\end{align*}
\hspace{1cm} (1.40)
\]

Where \(z\) is in km. Shreve also obtained expressions for the variation with attitude of the corresponding diffusivities (in cm\(^2\) sec\(^{-1}\)), for example,

\[
\begin{align*}
D_+ &= 3.6 \times 10^2 \ e^{0.092z} \\
D_- &= 4.8 \times 10^2 \ e^{0.092z}
\end{align*}
\hspace{1cm} (1.41)
\]

The values for \(Z = 0\) were obtained by substituting the corresponding mobilities and \(T = 273\)K.
1.10.2 ELECTRICAL STATES OF THE ATMOSPHERIC AEROSOL:

Aerosol particles acquire charge through Brownian deposition of ions. In term, such charged particles experience Brownian coagulation, which is enhanced or suppressed by electrostatic forces. Under fair weather conditions aerosol changing is approximately symmetrical, since small ions are created in air and have roughly equal mobilities. Therefore in equilibrium particles of any size have a charge distribution approximately symmetrical about zero charge, so that for every $V_j$ particles bearing charge $q_j$. Besides acquiring charge through ionic diffusion, aerosol particles polarized in the fair weather electric field and thereby received an additional ionic drift current.

1.10.3 CLOUD ELECTRIFICATION

1.10.3.1 MODELS FOR CLOUD ELECTRIFICATION:

There are a number of models for electrification of clouds. A few of them are given below:-

1. Convection charging
2. Particle charging by selective ion capture
3. Particle charging by thermoelectric effect.
4. Particle charging by induction
5. Non inductive charge transfer process
6. Electrification of thunder cloud by a entrainment mechanism of charge separation
7. Electrochemical charge separation in clouds.
1.10.3.1(a) CONVECTION CHARGING:

Vonnegut [58] independently proposed that a convective cloud may operate as an electrostatic energy generator according to the following scenario: Initially, an updraft carries positive space charge from the lowest levels of the troposphere into the growing cloud, the electric field cloud soon acquires a negative charge screening layer at its edges due to cloud particles capture of ions drifting from clear air to cloud under the influence of the main positive charge, finally, downdraft carry the negative charge closer to the ground thereby increasing the (reversed) electric field at the earth sufficiently to initiate positive point discharge which enhances the positive charges entering the cloud via the updraft. The continuance of this positive feed back cycle can thus provide for a strong buildup of electrostatic energy at the expenses of the organized cloud convective motions.

The time dependent model for cloud electrification has been developed [59] in which both convection and gravitational separation of charged precipitation particles work simultaneously towards its electrification. Not only the generated electric field but also the current density have been calculated for various values of precipitation intensely $P_o$, liquid water content $L$, rebound mean angle probability $<P>$, relaxation time $\lambda$, fractional constants of space charge and electric field $f_1,f_2$ and vertical air motion $U$. It has been found that an electric field of about $4.0 \times 10^5$ Vm$^{-1}$ and a current density of about $0.1 \mu$Am$^{-2}$ may normally be achieved for a vertical air motion $U \approx 4$ ms$^{-1}$
at a precipitation intensity of about 10 mmh$^{-1}$. However, occurrence of the first lightning flashes may also be explained even at precipitation intensity 5 mmh$^{-1}$ (taking $U \approx 8$ ms$^{-1}$). Thus it appears that the thunder cloud electrification may be explained by the combined precipitative and convective (CPC) charging mechanisms and the vertical air motion in the cloud plays an important role in its electrification.

1.10.3.2(b) PARTICLE CHARGING BY SELECTING ION CAPTURE:
Wilson [60] described how an electrically polarized cloud particle may selectivity capture ions of one sign as it falls. This happens, because while the lower surface of the particle may easily attract and capture ions which carry a sign opposite to the local surface charge, the upper surface is not as effective in this respect, since ions attracted to it must first catch up with it in order to be captured. The net effect of this selective process is a large scale separation of charge from due to the existing field, so that its occurrence in the cloud would cause a field enhancement in qualitative agreement with what is expected for thunderstorm.

Mathematical model for the "Wilson process" based on spherical particles in stokes flow has been worked out by Whipple and Chalmers [61]. The equilibrium charge for this process is proportional to the ambient field strength and particle surface area. Also, the process becomes ineffective for large fields, since then the ionic drift velocity greatly exceed drop terminal velocities. A simple estimate [62] suggest the mechanism may produce fields.
only as large as $100\text{Vm}^{-1}$, which is still three orders of magnitude below characteristics thunderstorm values.

**1.10.3.3 PARTICLE CHARGING BY THERMOELECTRIC EFFECTS:**

Reynolds *et. al.*, [63] obtained laboratory evidence that a Hail Pellet may become charged as a result of collisions with ice crystals having a temperature different from that of pellet. The physical basis of the charge transfer was suggested as being due to the diffusion of hydrogen ions down the temperature gradient existing in the region of momentary contact [64]. Thus, since $H^+$ ions have a greater mobility in the ice lattice than $OH^-$ ions, a temperature gradient maintained across a piece office will result in an excess of positive charge on the colder portion. Mason formulated a one dimensional model for this process on the basis of an ideal ice structure and found that magnitude of equivalent surface charge density $\sigma$ on the ends of an ice rod having prescribed steady state temperature gradient $dt/dx \text{ (°C. cm}^{-1})$ is given approximately by $\sigma \approx 5 \times 10^{-5} \frac{dT}{dx} \text{es.u.cm}^{-2}$, Similar results follow from a more complete theory of the process in the real ice having orientational defects worked out by Jaccard [65].

Apparently the results depend sensitivity on such factors as the time of contact, micro–topography of the areas of contact, presence of impurities in the ice, and the relative velocity impact. All of these factors are difficult to control in an experimental situation, and hence their effects are not easily evaluated.
1.10.3.4 PARTICLE CHARGING BY INDUCTION:

An uncharged drop polarized in the fair-weather electric field carries a surface charge density.

\[ \sigma \text{e.s.u.} = (4\pi)^{-1} (E_r)_{r=a} = 3e \cos \theta / 4\pi \]  

(1.42)

\( \theta \) being the polar angle measured from the lowest point on the drop; thus the lower hemisphere is positively charged, and the upper hemisphere negatively charged. Therefore, if such a drop were to experience on its lower hemisphere a momentarily electrical contact with, the subsequent separation from a similarly polarized smaller drop, there would result a net negative charge on the larger drop and a positive charge of equal magnitude on the smaller drop. The first to point out that such a process of inductive charge transfer occurring throughout a cloud and followed by the large scale separation of charge through relative sedimentation under gravity, would serve to increase the in-cloud electric field in the sense normally observed in thunderstorms.

1.10.3.5. NON INDUCTIVE CHARGE TRANSFER PROCESS:

These processes occur during particle collisions in which charge is transferred independently of the local electric field strength. It is perhaps unusual for a process to be named in terms of what it is not however, a more succinct and yet all encompassing little has yet to emerge. Beared and Ochs [66] use the term interface “charging” for charge transfer driven by differences in contact potential.
Detailed laboratory studies of the above charging process have been carried out over the last ten years. Jayaratne et. al., [67] confirmed that the sign of graupel charging reverses as a function of temperature and that this "reversal temperature" moves to higher (warmer) values with decreased cloud liquid water content. They also found that the amount of charge transferred depends on impact velocity and on the size of the small ice crystals used.

Keith and Saunders [68] extended the previous work by using larger ice crystals, up to 800 µm diameter, and found that the charge transfer increases rapidly with crystal size of small crystals but increases at a lower rate of larger crystals. They suggested that high values of charge transfer are limited by the reverse charge transfer of some of the charge residing on the surfaces when the particle in the dark. A study of crystal – graupel interactions in the dark revealed light emission associated with this reverse charge transfer in the form of corona [69].

From their charge transfer experiments; they formulated relationships between charge transfer, crystal size, and impact velocity for positive and negative charging situations.

1.10.3.6. ELECTRIFICATION OF THUNDER CLOUD BY A ENTERTAINMENT MECHANISM OF CHARGE SEPARATION:

Wagner and Telfold [70] proposed an entertainment mechanism for cloud electrification in which the micro scale charge separation can take place at the interface. This conductivity in homogeneity has been postulated to result either from the onset of ice process or from the evaporative depletion of
small ice or water particles in cloud particles, diluted by dry air entrained at the cloud top. They consider that the turbulence inside the thermals and the prevailing updrafts and downdrafts within the cloud are responsible for macro physical-charge separation. The ion pairs produced due to cosmic rays, as in the convective theory, provide the convective space charge in this mechanism, Sapkota and Varshneya [71] examined the extent to which the leakage current produced by the electrical forces acting on the descending thermals influences the net charge separation caused by the entertainment mechanism.
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