ICE NUCLEATION RELEVANT TO

FORMATION OF HAIL

by

Gabor Vali

ABSTRACT

Freezing nucleus contents of samples of rain and hail were
determined from the freezing temperatures of millimeter-sized drops
on a cold stage. Concentrations of nuclei in hail were found to be
higher than in rain. Ten to eighty percent of the nuclei are smaller
than 0.01μ in diameter. Nucleus spectra and proportions of small
nuclei in suspensions of surface soils are similar to those in
precipitation, suggesting soil origin of atmospheric nuclei. Capture
of small nuclei by diffusion to cloud droplets and collection of
large nuclei by falling precipitation can account for observed concen-
trations. Freezing temperatures of cloud droplets and raindrops were
derived. Estimated concentrations of ice pellets agree with reported
values. Concentrations of nuclei in updrafts were derived from water
budgets typical of large storms and the nucleus content of precipi-
tation: in hailstorms 100 nuclei per m^3 are active at -6 C, 1000 m^{-3}
at -10 C.

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SUMMARY

The freezing nucleus content of precipitation and its relation to the formation of ice in convective storms and to the nucleus content of the air in which clouds and precipitation develop have been investigated. Nucleus contents of samples of rain and of hail were determined from the freezing temperatures of millimeter-sized drops on a cold stage, and the concentrations are described in terms of differential and cumulative nucleus spectra. From ten to eighty percent of the nuclei were found, from filtration experiments, to be smaller than 0.01 μ in diameter. Nucleation temperatures are shown to be relatively stable properties of the particles.

The observed concentrations of nuclei in precipitation can be accounted for if it is assumed that nuclei smaller than 0.01 μ diameter are captured by diffusion to cloud droplets, and that the larger nuclei are collected by falling precipitation.

The freezing temperatures of cloud droplets and of raindrops are derived from the nucleus spectra of the precipitation.

The concentrations of nuclei in the cloud are estimated from the measurements on the precipitation and are found to be higher than indicated by previous measurements. The discrepancy is shown to be due to the inefficiency of cloud chambers for detection of small nuclei active at warm temperatures.

Surface soils were found to contain large numbers of freezing nuclei active at temperatures around -6 C, and comparisons with the nucleus contents of clay minerals indicate that the nuclei in surface soils originate in their organic and not in their mineral components. Similarities between the nucleus spectra of surface soils and the nucleus spectra of some hail and rain samples strongly suggest that the nuclei in these precipitation samples are of soil origin.

The flux of nuclei into a hailstorm is estimated to be of the order of 10^{10} sec^{-1} for nuclei active at temperatures warmer than -6 C, and 10^{12} sec^{-1} for nuclei active above -10 C. These estimates can serve to establish the requirements for artificial sources of nuclei if hail modification is to be attempted by augmentation of the natural concentrations of ice nuclei.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

When a liquid is cooled, the temperature at which freezing commences
is always lower than the melting temperature. The theoretical work of
Gibbs (1906) and of Volmer (1929) showed that the initiation of freezing
by the formation of singularities in a homogeneous liquid can be expected
to occur only at temperatures well below the melting point. Although
observations show that water seldom remains unfrozen at temperatures
colder than a few degrees below 0 C, freezing temperatures can be lowered
for given specimens of water by the removal of suspended impurities.
It is also observed that when any volume of water is divided into smaller
volumes, the freezing temperatures of most of the portions are lower than
the freezing temperature of the whole, cloud droplets often remaining
unfrozen at temperatures as cold as -40 C. It has therefore been con-
cluded that freezing in most cases is attributable to the presence of
foreign bodies, and that varieties of nucleating particles exist, those
capable of initiating ice formation at small supercoolings being less
abundant than those active at lower temperatures. Nucleation by impur-
ities is said to be heterogeneous and nucleation in pure substances is
said to be homogeneous.

Nucleation involves the cooperative action of a fairly large
number of water molecules under the influence of the nucleating substrate,
and cannot be treated adequately by the methods of molecular physics.
Theoretical analyses of nucleation have therefore been restricted to
a thermodynamical approach relating nucleation probability to the free
energy of formation of ice embryos. This approach provides only

a gross description of the nucleation of ice, which experiments show
to be strongly influenced by the chemical and surface properties of
the substrate. At present, nucleation of ice cannot be discussed
theoretically in terms of concentrations and types of impurities in
the water; direct measurements are necessary. However, although the
formation of ice is readily observable, it has not been found possible
so far to unambiguously determine where the nucleation occurs. Most
current research, including this thesis, is therefore concerned with
the determination of the frequencies with which nuclei of differing
degrees of effectiveness occur in air or in water, and tries to
establish some relation between this nucleus content and the character-
istics of the aerosol or the suspended particles.

The nucleus content of air is usually determined by observing the
number of ice particles that develop when a cloud is formed in a cloud
chamber. The nucleus content of water is found by observing the freezing
temperatures of large numbers of drops. There are difficulties in both
types of measurements. In cloud chambers the activation of nuclei is
influenced by a multitude of experimental variables, such as supersat-
uration, cloud droplet sizes and concentrations, the length of time the
temperature of activation is maintained, and others. In addition it is
uncertain whether the formation of ice in cloud chambers is initiated
by sublimation or freezing. The droplet-freezing experiments have to
cope with the fact that only one nucleus per drop can be detected,
although invariably each drop contains a variety of nuclei of differing
activities, but at least these experiments are unambiguous as to the
mode of ice formation.

For the study of atmospheric processes cloud chamber measurements have been generally preferred, chiefly because of the supposed similarity of the experiments to natural processes. However, because of the uncertainties mentioned above, it has been difficult to assess the adequacy of the simulation of natural conditions. Agreement between the results of these measurements and the observed behaviour of clouds is not notably good, with especially large discrepancies at temperatures not far below 0 C.

The work reported in this thesis was undertaken to establish the relation between the nucleus content and the freezing temperatures of drops of water, and to investigate the possibility of determining the freezability of cloud water from the nucleus content of precipitation. This approach seemed to offer two advantages: Drop-freezing experiments can provide information on nuclei active at temperatures close to 0 C, and results that reflect conditions in the active regions of the clouds are obtained. Formation of ice at relatively warm temperatures is generally thought to be an important factor in the development of hail; the results would therefore have especial relevance to hail studies.

Freezing has been studied by droplet experiments for both the homogeneous and heterogeneous nucleation of metals (Vonnegut, 1948), polymers (Burns and Turnbull, 1966), water (Dorsch and Hacker, 1950; Bigg, 1953; Langham and Mason, 1958; Hoffer, 1961, among others), and other substances. For homogeneous nucleation the interpretation of the experiments in terms of the rate of formation of critical embryos and the stochastic nature of the process can be given. If nucleation

is due to suspended impurities the freezing temperatures of the drops
are determined by the statistical distribution of nuclei of various
degrees of effectiveness among the drops and by the temperature-depend-
ence of the probability of nucleation for each nucleus. It was shown
by Vali and Stansbury (1966) that for a given nucleus the probability
of nucleation increases sharply as the temperature is lowered through
a temperature characteristic of the nucleus, so that to a first
approximation the nucleus can be said to nucleate at its characteristic
temperature. From the observed freezing temperatures of drops one can
therefore find the concentrations of nuclei of differing characteristic
temperatures, that is the nucleus spectrum (Vali, 1967, and Chapter III).
The nucleus spectra of samples provide complete descriptions of the
nucleus content and permit meaningful comparisons between samples.
From these spectra the freezing temperatures of drops of any size can
be found. Therefore, if the spectra of precipitation samples are
determined, estimates of the freezing temperatures of cloud droplets
and of raindrops can be made.

It was known from previous work (Barklie, 1960; Stansbury, 1961),
and confirmed in recent measurements, that the concentrations of nuclei
active at temperatures warmer than -10 C are frequently found to be
quite high in precipitation samples, more frequently in hail than in
rain or snow. The degree of cloud glaciation that these nucleus concen-
trations imply has been worked out by Hitschfeld and Douglas (1963) on
the basis of the stochastic theory of nucleation (Stansbury, 1961).
The description of nucleus content in terms of the nucleus spectra
required a re-examination of these results.

Another relevant property of nuclei is their size or diameter. Nucleus is of significance not only from the point of view of basic understanding of the nucleation process, but also because the processes by which nuclei enter the precipitation are strongly dependent on the sizes of the particles. Previous research had indicated that nuclei were about $0.1\,\mu$ in diameter. Particles of $0.1\,\mu$ to $1\,\mu$ diameter are removed from the air least efficiently however (Greenfield, 1957); the high nucleus concentrations in precipitation seemed to be incompatible with this. It was therefore desirable to determine experimentally the sizes of the nuclei in precipitation samples. Recently, attempts have been made to identify the nuclei of snow crystals and to measure their sizes directly by electron microscopy (Byers, 1965). Such methods would be very unreliable for the detection of nuclei among the many particles present in a drop; the observation of changes in nucleus content that result from the removal of particles larger than certain selected sizes seemed therefore to be a more practical approach.

The plan for this work was to determine the concentrations and sizes of freezing nuclei in precipitation and to construct a model to account for these observations in terms of the capture of the nuclei by cloud droplets and precipitation. In Chapters III to V the experimental results on the general properties of freezing nuclei and on the nucleus content of the precipitation are presented. The factors influencing the transfer of nuclei from the air into the precipitation are discussed in Chapter VI and the distribution of nuclei in space and time are examined in Chapter VII. The estimated glaciation of clouds is described in Chapter VIII and the concentration of nuclei

in air, inside clouds, is estimated in Chapter IX.

Freezing due to suspended particles is the only glaciating mechanism considered; the results therefore represent estimates of the contribution made by freezing nucleation to the overall glaciation, but the roles of other processes have not been clearly demonstrated so far. There is evidence, however, that freezing occurs more readily than sublimation at small supercoolings (Bryant et al., 1959; Mason and van den Heuvel, 1959; Maybank and Barthakur, 1966; Isaka and Soulage, 1966), and the available in-cloud observations are found to be in reasonable agreement with the predictions of the model here developed.

II.   TECHNIQUES AND PROCEDURES

The experimental technique employed in this work is a development of that described by Stansbury (1961) and Vali (1964).   Small modifications only have been made, so that the earlier and the more recent measurements are all comparable and constitute a large body of observations; the internal consistency of the various aspects of these observations permits considerable confidence to be placed in the results.   The principal merits of this experimental approach are that the observations of freezing events are clear-cut at any temperature, and that experimental conditions are defined by temperature alone.

The nucleus content of water samples is determined in these experiments from the freezing temperatures of drops produced from the sample.   The drops are placed on a coated metal surface, the temperature of which is gradually lowered until all drops are frozen.   One hundred to three hundred drops of 1 to 2 mm diameter are frozen for each sample, so that samples of 2 cm^3 or more are necessary.   From 50 to 150 drops are produced by dispensing water from a syringe and are arranged in a regular array upon a cold stage of 36 cm^2 working area. The surface in contact with the drops is a film of silicone varnish[*]

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[*] General Electric Co.   Dri-Film No. 88.   In earlier experiments a hydrocarbon oil was used; identical results are obtained with the use of either surface.   The change has been made only because the silicone is more hydrophobic and thus if water condenses from the air onto the surface, between the drops, this condensate forms tiny droplets rather than a film of water, and the possibility of ice spreading along the surface is reduced.   Some freezing of the condensed droplets is observed at temperatures below -30 C which is beyond the range of temperatures used.   Drying of the air in the apparatus thus becomes unnecessary.

which is applied as a solution onto a thin sheet of aluminium covering

the cold stage. A new surface is prepared for each new set of drops.

The cold stage is cooled by thermoelectric heat pumps; the rate of

cooling is 2 deg min^{-1} at all temperatures. A photographic record

is made of the array of drops after every 0.2 deg decrease in temperature.

The accuracy of the temperature sensors and indicators is ±0.1 deg.

The absence of influence from the supporting surface on the

freezing temperatures of the drops was demonstrated by refreezing

drops after they had been moved to new positions on the surface. The

drops were frozen, then melted, shifted to new positions and frozen

again. The correlation between the first and second freezing tempera-

tures of drops was found to be the same as that for drops refrozen with-

out change in position (cf. Chapter IV, Section 3). Contamination of

the drops from the air was found to be negligible; drops which were

unfrozen when a temperature of -20 C was reached remained unfrozen for

hours while the temperature was maintained at -20 C.

Only plastic storage containers, syringes and filter holders were

used. Containers were not reused; syringes and filter holders were

boiled in distilled water and rinsed before using for a new sample.

Stainless steel syringe needles were cleaned in similar manner. Syringes

and needles, and filter holders if used, were tested by using them to

produce a number of drops of distilled water which were then frozen

simultaneously with drops from the sample under investigation.

Precipitation samples were collected in Montreal and in Alberta,

where a network of collectors (112 stations over a 3600 sq mi area)

as well as a mobile sampling unit have been operated for one season.

One of each type of plastic collector used was tested in the laboratory by simulating rainfall with distilled water and measuring the nucleus content of the sample obtained. No appreciable contamination was apparent. The collectors were kept sealed while in the field and were to be uncovered only whun precipitation was occurring at the station. Samples were frozen in the container in which they were received immediately after collection. They were transported in the frozen state to the laboratory where they were melted just before analysis. No changes in nucleus concentrations with time could be detected for samples kept frozen, and the rate of change for melted samples, at temperatures below 10 C, was found to be small enough to produce negligible changes only over the few day period the melted samples were stored (cf. Chapter IV).

Further details of specific experimental procedures are described at relevant places in the following chapters.

III.   DERIVATION OF NUCLEUS SPECTRA FROM DROP-FREEZING EXPERIMENTS

The basic observation in an experiment in which drops of equal
volume and of the same sample of impure water are cooled to temperatures
below 0 C is that the drops all freeze at different temperatures, with
an apparently random spread of freezing temperatures over a range of
several degrees. The factors influencing the freezing temperatures
are the origin of the sample, the volume of the drops, and the rate of
cooling.

It was shown by Vali and Stansbury (1966) that in heterogeneous
nucleation the rate of cooling is a relatively minor factor (over the
range 0.5 to 10 deg min^{-1}), with the average freezing temperatures of
samples changing less than 1 deg for a tenfold change in the rate of
cooling, and therefore as a first approximation freezing temperatures
can be considered time-independent. The negligible time-dependence
of freezing temperatures signifies that molecular fluctuations are of
secondary importance in determining the temperature at which ice stably
forms on a nucleating particle, the nature of the nucleus providing the
dominating influence.

With large numbers of particles of varying nucleating abilities
present in a sample of water, the freezing temperature of a drop of
water is determined by the most effective nucleus (i.e. the nucleus
with warmest nucleating temperature) that was apportioned to that drop
by chance on division of the water into drops. By observing the freezing
temperature of a drop, one therefore obtains information on only one
nucleus in that drop, all other nuclei remaining undetected. Observation

of the freezing of many drops is thus required in order to find the
concentrations of nuclei of differing characteristic temperatures,
i.e. the nucleus spectrum. The nucleus spectrum can be obtained from
the freezing temperatures of drops on the assumption that the fraction
of unfrozen drops that is observed to freeze in a given temperature
interval represents the fraction of all drops, frozen and unfrozen,
that contain a nucleus active in that temperature interval. This
assumption implies that the probability of finding a nucleus of a
certain type in a drop is the same for all drops and independent of the
presence of other, more active, nuclei. Drops that are already frozen
at the temperature in question froze due to the presence of more active
nuclei, but this affects only the possibility of detection and not the
presence of the less active nuclei. If $N(\theta)$ denotes the number of
unfrozen drops at temperature θ (Celsius), the fraction, $-\Delta N/N$, that
freezes when the temperature is decreased by $\Delta\theta$ should equal the number
of nuclei per unit volume active in a one degree interval, $k(\theta)$, times
the volume of the drops, V, times $\Delta\theta$:

$$ - \frac{\Delta N}{N} = k(\theta) \cdot V \cdot \Delta\theta \tag{1}$$

The nucleus spectrum, $k(\theta)$, can thus be obtained from the observed
quantities ΔN, $\Delta\theta$ and N. This nucleus spectrum is referred to in the
following as a differential spectrum to distinguish it from the cumu-
lative spectrum which describes the concentrations of nuclei active at
temperatures warmer than the temperature considered.[*]

[*] This distinction has not been made in the previous literature. The
nucleus spectra derived from cloud chamber experiments are cumulative
spectra since by counting the number of crystals developing in the
chamber at some temperature θ, the count includes nuclei active at all
temperatures warmer than θ. Differential spectra cannot readily be
obtained from cloud chamber measurements.

The cumulative spectrum, $K(\Theta)$, can be obtained by integrating equation (1) to yield

$$K(\Theta) = -\frac{1}{V} \ln \frac{N(\Theta)}{N(0)} \tag{2}$$

where $N(0)$ stands for the total number of drops in the sample. Equation (2) is identical in form to the expression that would result from considering $K(\Theta)$ as the probability that at least one nucleus active at some temperature above Θ will be found in a drop of volume V, and equating this probability to the fraction of drops that are observed to be frozen at Θ.

The two types of spectra, differential and cumulative, have different uses: the differential spectrum gives information on the types of nuclei in the sample, the cumulative one describes the freezing of a sample as it is cooled from 0 C (as it invariably is) towards colder temperatures. Consequently, when discussing the nucleus content of a sample, the differential spectrum will be used, but when the freezing temperatures of drops are to be found, the cumulative spectrum provides the necessary information.

Figure 3-1 (b) and (c) show examples of the two types of spectra for a sample of 162 drops of melted hail. These were calculated from the observed distribution of freezing temperatures which is presented in Fig. 3-1 (a) as a histogram.

The values plotted for the differential spectrum have been smoothed by taking the running mean of the concentrations calculated for three adjacent temperature intervals (of 0.25 deg). The cumulative spectrum is obtained by summation of the non-smoothed concentrations. The
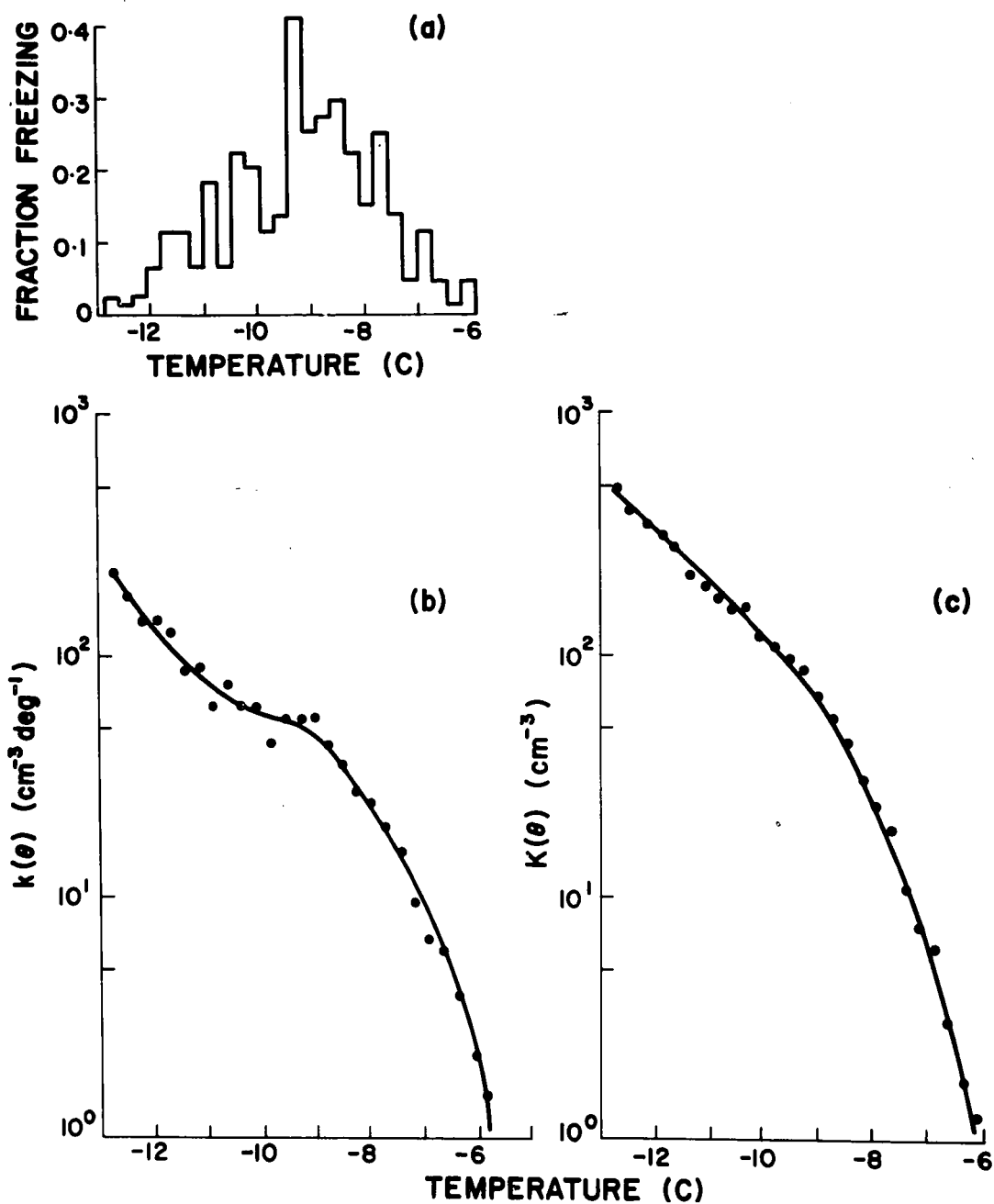
Figure 3-1.   (a) Distribution of freezing temperatures
for 162 drops. (b) Differential nucleus spectrum,
derived from the data in (a). (c) Cumulative nucleus
spectrum.

curves in both cases were fitted subjectively. Objective methods
for fitting curves are not readily applicable, because of the different
statistical significance of each point. Each point for such spectra
is obtained from a ratio: $\Delta N/N(\theta)$ or $N(\theta)/N(0)$ for the two types
of spectra respectively. The values of ΔN are usually small when
small temperature increments (0.25 deg) are chosen and are especially
small at the extremes of the temperature range of the freezing events;
$N(\theta)$ is small at the lower end of the temperature range. The statis-
tical significance of the points is consequently highest in the middle
portions of the spectra. The spectra were fitted to the points with
these factors taken into consideration, especially in cases where
narrow peaks or dips occurred in the spectrum.

By increasing the number of drops used for a given sample, the
resolution of the nucleus spectra can be improved and the uncertainties
in the nucleus concentrations can be reduced. In order to establish a
reasonable compromise between sample size (number of drops) and accu-
racy of nucleus spectrum, computer-simulated experiments for 72, 180,
600 and 3000 drops were performed for an assumed nucleus spectrum.
Figure 3-2 shows the arbitrary nucleus spectrum and the results for
different numbers of drops. As indicated by this graph, a spectrum can
be determined with fair reliability from as few as 72 drops and improve-
ment in resolution is slow with increasing numbers of drops. In general,
no less than 150 drops were used in the experiments for which results
are reported in the following chapters.

Ten computer-simulated spectra, for 150 drops each, were found to
lie within the band shown in Fig. 3-3; the boundaries given are the
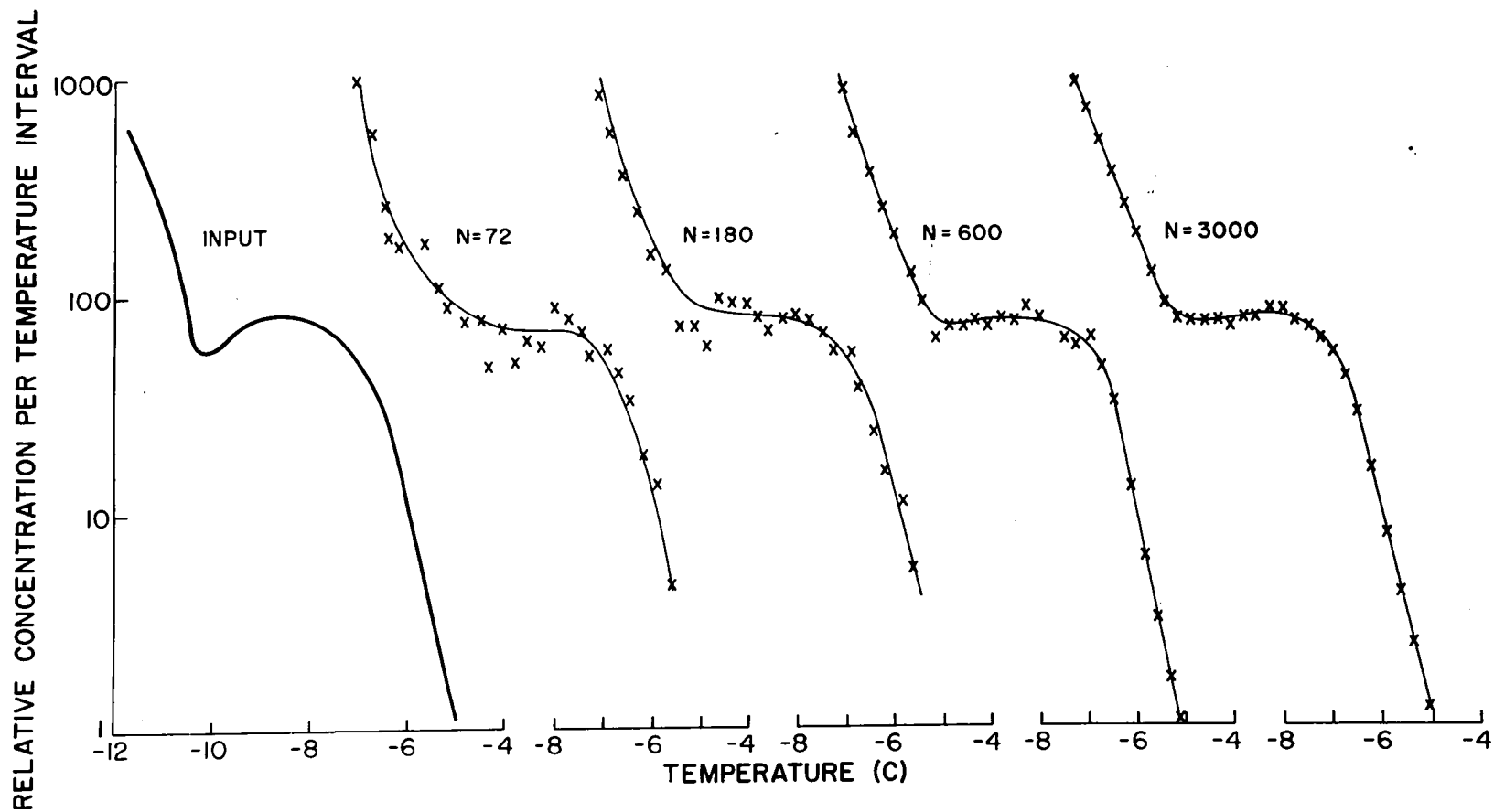
Figure 3-2. Nucleus spectrum and simulated experimental
results for samples with different numbers of drops (N).
Thin lines were fitted subjectively.

envelopes of the lowest and highest values at all temperatures. The

maximum variation in concentrations occurs at the warm temperature

end of the spectrum, whereas the maximum range in temperatures for a

given concentration to be reached is in the middle part of the spectrum.

Similar experiments for a simple exponential spectrum resulted in ten

spectra that were all within a factor of 1.35 of one another at all

temperatures. The degree of confidence that can be placed in the

concentrations indicated by a spectrum is thus seen to be dependent on

the shape of the spectrum. In general, differences of about a factor

1.5 or greater can be said to reflect true differences if present over

Figure 3-3. Envelopes for minimum and maximum concen-
trations given by ten simulated experiments.

Figure 3-4.   Extended nucleus spectra for samples of
hail.   Original and 100 times diluted samples were used
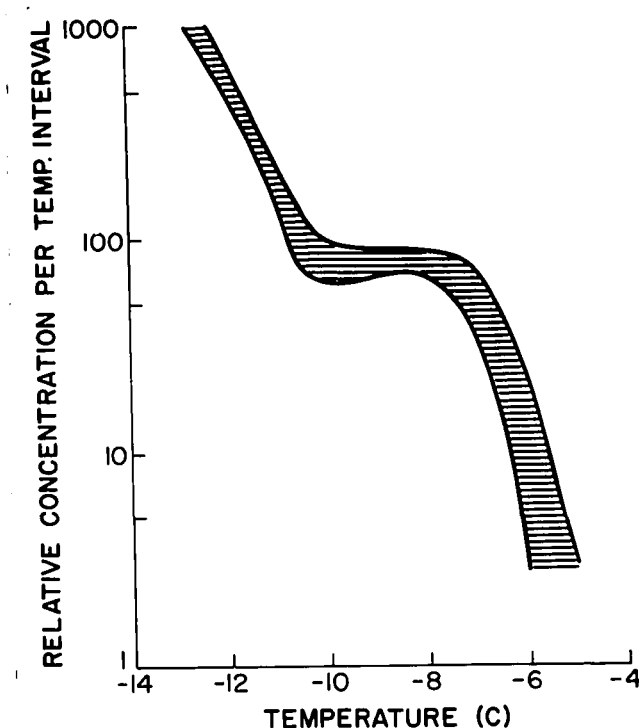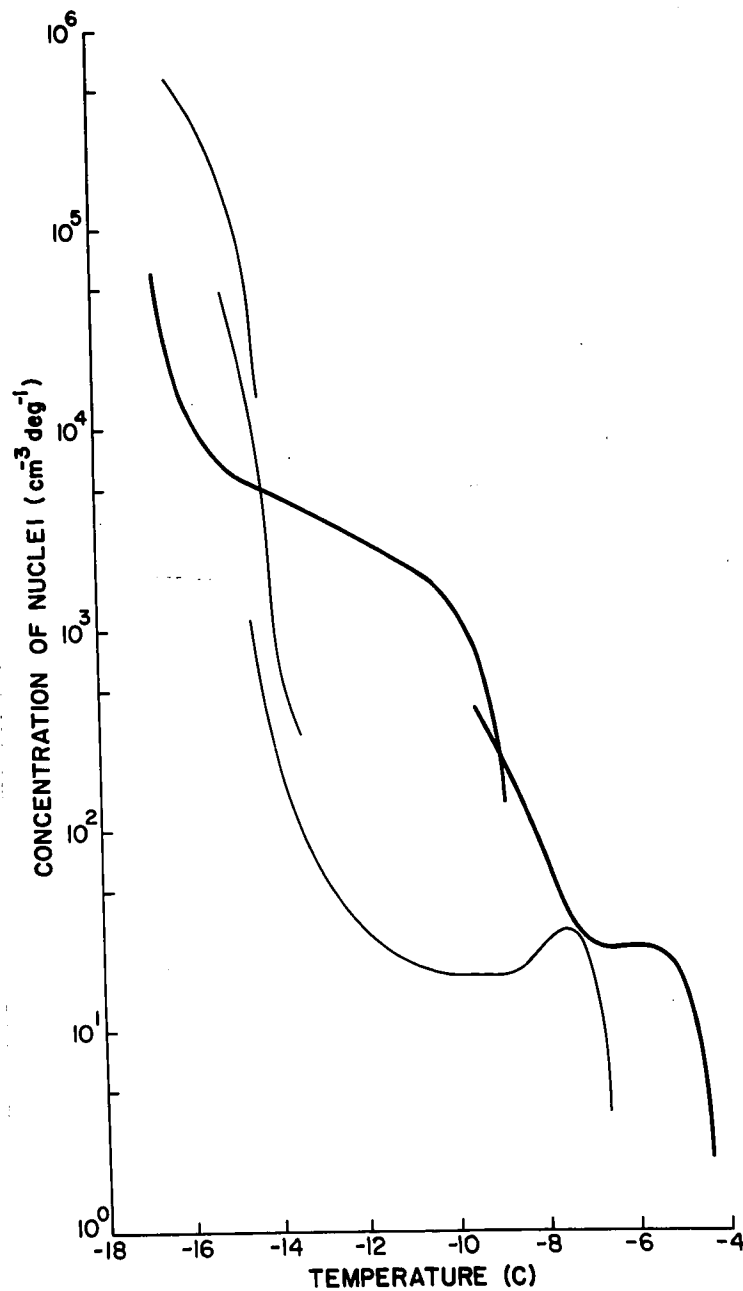to obtain curves for 10^0 to 10^2 and 10^2 to 10^4 cm^{-3} deg^{-1}
nucleus concentrations respectively.

fairly large portions of the spectra. Over small intervals, only differences exceeding factors of 3 or 4 are reliable when the spectra are based on 100 to 300 drops.

The majority of experiments have been performed with drops of 0.01 cm^3 volume (2.7 mm equivalent diameter) and with approximately 150 to 250 drops per sample; the values were chosen for experimental convenience and expediency. With such experiments, nucleus concentrations between 10^0 cm^{-3} deg^{-1} and 3 x 10^2 cm^{-3} deg^{-1} are detected. In order to extend this range towards higher concentrations, drops of smaller volume or diluted samples must be used. Reduction of the drop size below 10^{-3} cm^3 (1.2 mm diameter) is not possible with the present experimental arrangement, and therefore only a one decade extension can be achieved this way. Dilution with distilled water can be used to find concentrations of any magnitude but only at temperatures above that at which the concentrations of nuclei of distilled water become dominant.

Figure 3-4 shows nucleus spectra for two hail samples in which extensions towards higher concentrations have been obtained by the use of 1% dilutions of the original samples. In addition, small drops of the diluted sample were used in one case to obtain a further extension of one decade. The gap which appears systematically at the junctions of the spectra is caused by inaccuracies in the volumes of the drops, which result in overestimates of low concentrations and underestimates of high nucleus concentrations when the concentrations are calculated on the basis of nominal drop volume.

Extensions of spectra towards lower concentration can be obtained

by the use of larger numbers of drops or drops of larger volume.

Partial evaporation of water has been unsuccessful as a means of

increasing the nucleus concentrations. Increasing the number of drops

is difficult, as a tenfold increase in the number of drops frozen would

be required for each decade of extension of the spectrum. Experiments

with large drops are also inconvenient due to the limited size of the

cold stage and the small number of drops that can be handled simultane-

ously. In addition, the temperature gradients across large drops become

appreciable and lead to uncertainties in the nucleation temperatures.

In a few cases such experiments were performed; Fig. 3-5 shows the

results of one experiment in which 162 drops 0.01 cm^3 in volume

(in 2 runs) and 189 drops 0.2 cm^3 in volume (in 21 runs) from a sample
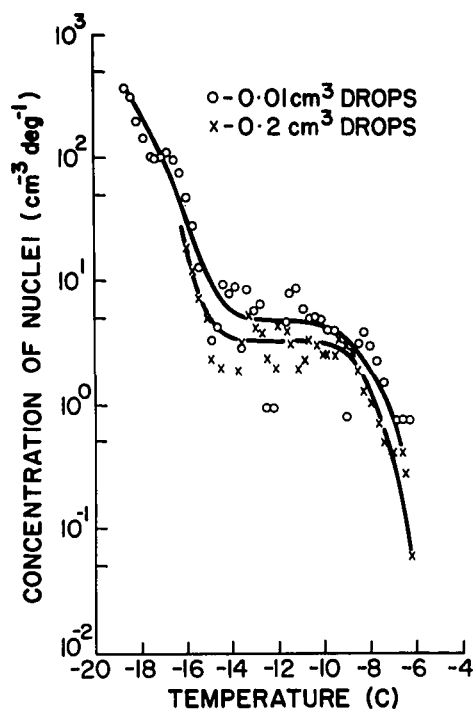
Figure 3-5. Nucleus spectra obtained with 0.01 cm^3 and with 0.2 cm^3 drops for sample of rain.

of rainwater were frozen. The two spectra differ by a factor two, uniformly over the range of temperatures where the two curves overlap. No explanation has been found for this discrepancy; in part it may be due to inaccuracies in the volumes of the drops.

In summary, it has been shown that the concentrations of freezing nuclei of different temperatures of activity can be determined from drop-freezing experiments. Concentrations between 10^{-1} cm^{-3} deg^{-1} and 10^3 cm^{-3} deg^{-1} can be measured by using 100 to 300 drops of 10^{-3} cm^3 to 10^{-1} cm^3 volume; higher concentrations can be measured for nuclei active above -22 C by dilution. The nucleus spectra provide complete descriptions of the concentrations of nuclei and permit meaningful comparisons betweeen samples.

IV. PHYSICAL PROPERTIES OF FREEZING NUCLEI

Freezing nuclei are observed in the drop freezing experiments through their action. Clearly, it would be most desirable to identify these nuclei as well, and to determine their physical and chemical natures. Direct identification and analysis of the nuclei is not feasible, however, because freezing nuclei can be smaller than $0.01\,\mu$ in diameter, and the total number of particles of comparable sizes in a typical sample of water may be 10^{10} to 10^{12} times greater than the number of freezing nuclei active at -10 C. The evidence for the small sizes of the nuclei is presented in Section 1 of this chapter, and their rarity is examined in Section 2.

The reproducibility of the temperature at which a given nucleus becomes effective has been tested. The results given in Section 3 point to the fact that nuclei retain their effectiveness over considerable periods of time (while exposed to air, suspended in water or frozen into ice) and over numerous cycles of freezing and melting.

Experiments with a small number of soil samples revealed unexpectedly high nucleating abilities for certain surface soils. These results, and evidence that some components other than the basic clay minerals are the nucleating substances in the soils, are presented in Section 4.

1. SIZES OF FREEZING NUCLEI

It has been generally believed that atmospheric ice nuclei are about $0.1\,\mu$ in diameter, and that $0.02\,\mu$ is the smallest particle capable of promoting ice formation at temperatures warmer than -10 C. Theoretical considerations by Fletcher (1958, 1966) and by Miloshev and Krastanov (1965),

as well as experiments by Kumai (1951) and others have pointed to such a conclusion.

The theoretical approach is to calculate the frequency with which ice embryos of critical size appear on the nucleus with the assumptions that nuclei are spherical particles, and that the interface energies are known. Figure 4-1 shows the results of such a calculation for nucleation from supercooled water. The surface parameter m is defined by the relation

$$m = \frac{\sigma_{NW} - \sigma_{NI}}{\sigma_{IW}}$$

where σ_{NW}, σ_{NI} and σ_{IW} are the interface energies of nucleus-water, nucleus-ice and ice-water surfaces respectively.
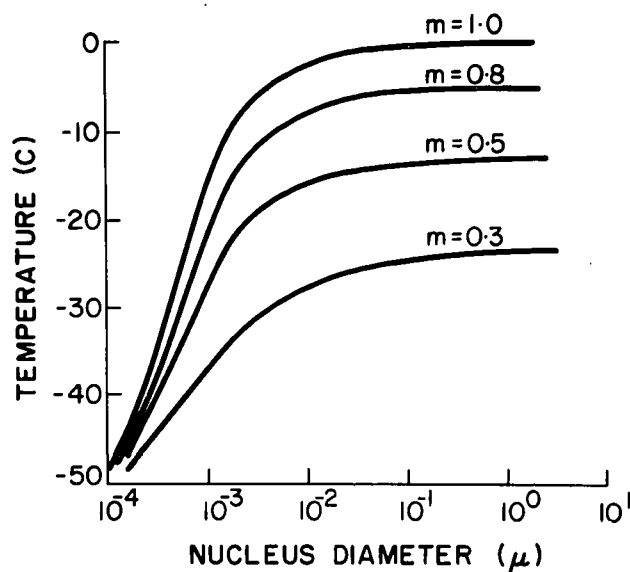

Figure 4-1. Temperature at which a spherical nucleus of given diameter and surface parameter (m) will nucleate ice from water in one second. (After Fletcher, 1966)

According to this graph, particles below about $5 \times 10^{-3} \mu$ diameter rapidly lose effectiveness (nucleate at colder temperatures) with decreasing particle size, but the loss in activity when particle diameters decrease from $10^{-1} \mu$ to $10^{-2} \mu$ is only a few degrees. The limitations of this theoretical approach have been summarized by Fletcher (1966). The main difficulty is that the chemical bonding and crystallographic factors that would have to be taken into account in order to calculate the interface energies from first principles are not well known. These difficulties are compounded by the fact that one is really interested in the values of the relevant parameters over regions comparable in size with the size of the critical ice embryo, and such small scale local situations might be significantly different from ideal surfaces. The usefulness of the thermodynamic theory of nucleation in its present state of development is consequently rather limited.

A number of investigators have attempted to identify the nuclei responsible for the formation of natural and artificial snow crystals, by locating the large central particles (where such were to be found) in the crystals. Summaries of such observations were given by Byers (1965) and Dufour (1966). The particles found in the crystals were mostly of clay minerals and were between 0.1μ and 10μ in size. However, the fact that these particles, rather than one of the many smaller particles which were invariably present, were the nuclei responsible for the formation of the crystals has not yet been firmly established.

Georgii and Kleinjung (1967) reached the conclusion that atmospheric ice nuclei active at -21 C are between 0.4μ and 4μ in diameter

from a long series of daily measurements of the concentrations of ice nuclei, large particles ($>0.1 \mu$) and of Aitken nuclei. A cloud chamber, an impactor and an expansion chamber were used for the three types of measurements respectively. The concentrations of ice nuclei and the concentrations of large particles were found to vary in closely parallel fashion, whereas no correlation between Aitken nucleus and ice nucleus concentrations was evident. On the other hand, Langer (1967) and Rosinski (1967) have found that in measurements obtained with continuously recording equipment, the correlation between ice nucleus concentrations and Aitken nucleus concentrations appeared to be better than between ice nuclei and large particles. The contradictions of these findings and the reservations that are expressed in Chapter VII regarding the efficiency of cloud chambers for the detection of small freezing nuclei render these results inconclusive.

Bigg and Meade (1959) used a continuously operating cloud chamber with the input air alternately passed into the chamber directly or through three different sedimentation boxes. The latter were designed to remove particles greater than 1.6 μ, 4 μ and 22 μ diameter respectively. By this method 30% of nuclei active at -18 C were found to exceed 4 μ diameter and 40% were larger than 1.6 μ. However, these results must be held inconclusive, because the sedimentation boxes, in addition to removing particles above a certain size by sedimentation, also remove particles smaller than about 0.1 μ diameter by diffusion of the particles to the plates.

In order to obtain information on the sizes of the freezing nuclei whose activity is observed in the drop freezing experiments, filtration

experiments were conducted in which the nucleus content of samples of water was determined after the samples were passed through filters of various pore sizes.

Membrane filters (manufactured by Millipore Ltd.) were used in plastic holders. The filters are made of mixed esters of cellulose, and have nominal pore sizes from 0.01μ to 8μ for the different types. Pore sizes are specified by the manufacturer on the basis of a mercury intrusion measurement and the stated variations are $\pm10\%$ for 0.1μ pore filters and $\pm20\%$ for the 0.01μ pore filters. Eighty percent of the filter volume is taken up by the pores which go from one surface to the other in a winding path.

The filter holders were attached directly to the syringes used to produce the drops on the cold stage. In this way a minimum of extra handling was necessary. Control runs, using distilled water, showed no discernible increase in the concentration of nuclei due to contamination from the holder.

The efficiency of the filters for the capture of aerosols has been measured by Megaw and Wiffen (1963) and found to be 100% for particles greater than the pore size and also for particles below 0.02μ in diameter. The tests were made with a 0.8μ pore size filter. The small particles are thought to be caught by diffusion to the walls of the pores. No data is available for the performance of these filters in water, and therefore it will be assumed in the following that particles larger than the nominal pore size are retained and all particles smaller than the pore size pass through. The filter will, in fact, retain some of the particles which are smaller than the pore size; the fraction retained

could become appreciable if the concentration of large particles in the water were high and the pores became partially obstructed. Increases in the pressure required to produce flow through the filters indicated that clogging was occurring on some occasions. Loss by attachment of the small particles to the intricately curving walls of the pores could also be appreciable.

In order to evaluate the performance of the filters, a sample of soil suspension, from which large particles were allowed to settle out, was tested after one and after two filterings with $0.01\,\mu$ pore size filters. Figure 4-2 shows the nucleus spectra obtained.
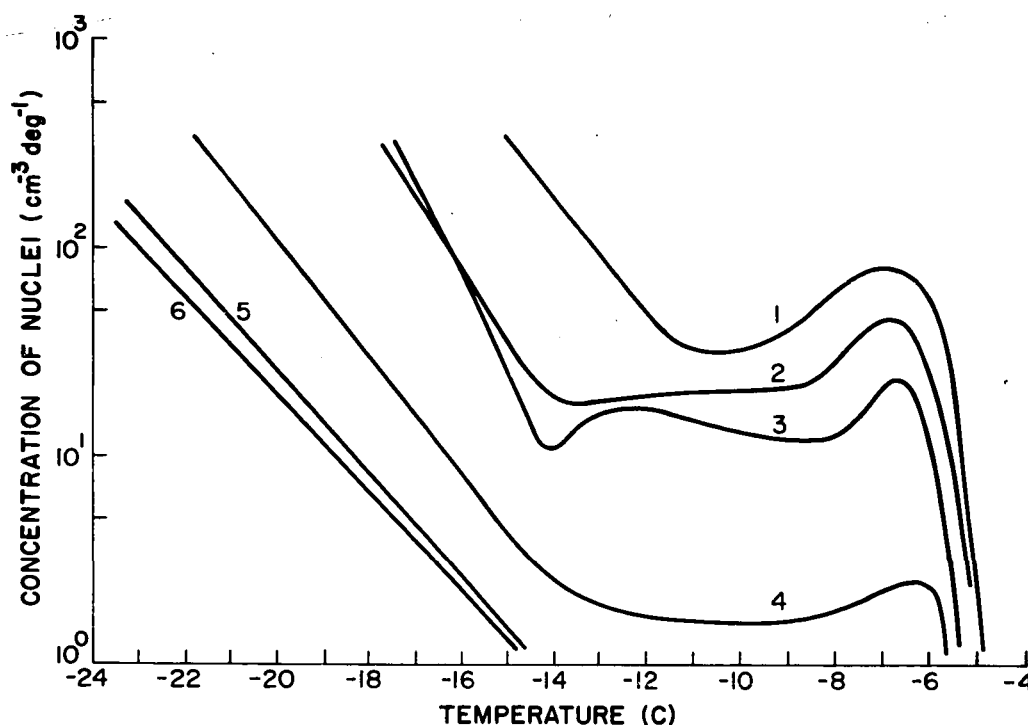

Figure 4-2. Nucleus spectra for unfiltered and filtered samples. Curves 1 to 3: soil suspension without filtering and after one and two filterings with $0.01\,\mu$ pore size filters. Curve 4: distilled water rinse of second filter. Curves 5 and 6: unfiltered and filtered distilled water.

Curves 1, 2 and 3 are for the unfiltered, once-filtered and twice-filtered samples respectively. The second filter, after use, was reversed in its holder and distilled water passed through it; the nucleus spectrum for the rinse water is shown in curve 4 in Fig. 4-2. These spectra show that the second filtering produced about 50% reduction in nucleus concentrations at temperatures above -10 C. Therefore, the concentrations of nuclei smaller than 0.01μ in the original sample may have been twice as high as shown by the spectrum obtained after the first filtration, although this would then mean that all the nuclei in this sample were smaller than 0.01μ (for temperatures above -10 C). At temperatures colder than -12 C, the reduction in nucleus concentration produced by the first filtration was greater, and that produced by the second filtration smaller than at temperatures above -10 C. The first reduction indicates that larger proportions of these nuclei were greater than 0.01μ, than for nuclei active above -10 C. The differences in the observed reductions of nucleus concentrations on second filtering for the different temperature ranges cannot be explained on the basis of particle size alone. Generally, the results shown in Fig. 4-2 indicate that there is no sharp lower limit in particle size for the retention of particles by the filter, and therefore in the unfiltered samples concentrations of particles (or nuclei) smaller than the pore size are higher than the measured concentrations indicate.

Figure 4-2 also shows the nucleus spectra for unfiltered and filtered distilled water (0.01μ filter). The change in concentration is less than a factor 1.5, which is comparable to the experimental uncertainty for samples of the size used.

Both sets of curves shown in Fig. 4-2 show a feature that has been found to be common to all samples tested: no systematic difference exists between the warm and cold ends of the nucleus spectra with respect to the reduction that is obtained on filtering. Thus it is found, that nuclei active at the warmest freezing temperatures observed can also be as small as 0.01 μ . This result clearly contradicts the theoretical predictions given by Fig. 4-1. Due to the steepness of the measured spectra at the warm end, it is difficult to assess whether or not the argument can be extended to temperatures above -5 C.

A number of samples were tested by filtering portions of these with 1.2 μ , 0.1 μ and 0.01 μ filters. The concentrations of nuclei in the filtered samples were observed to decrease with decreasing pore sizes of the filters. An example is shown in Fig. 4-3.
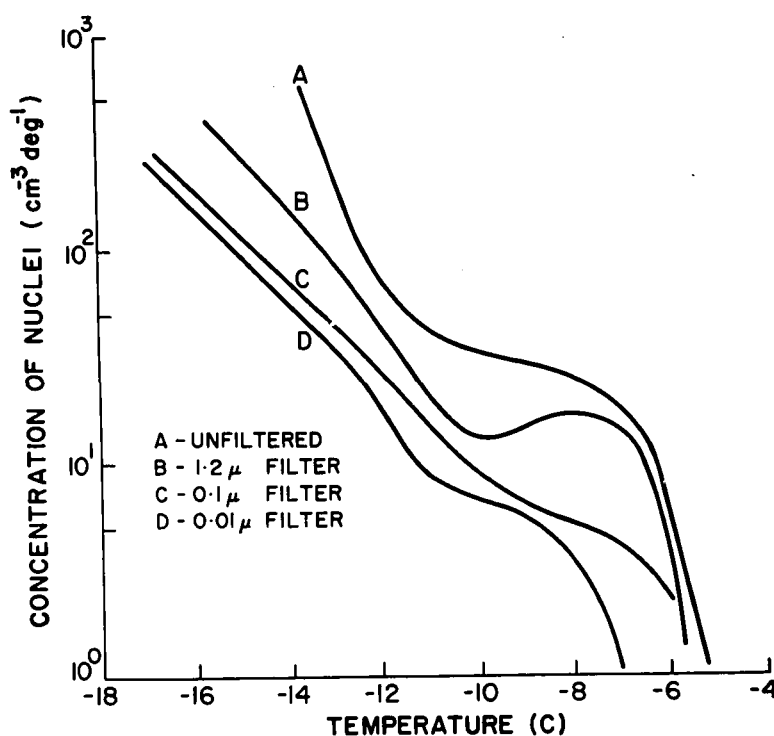
Figure 4-3. Nucleus spectra for a sample of hail after filtration with filters of different pore sizes.

These experiments confirm the absence of any direct relation between the sizes and the effective temperatures of freezing nuclei over the ranges involved, in that no upper temperature limits become apparent when the nucleus sizes are limited by an upper threshold (the filter pore size).

For the majority of samples, only the unfiltered sample and a part filtered with a 0.01 μ pore size filter were tested. Figure 4-4 shows three pairs of nucleus spectra for a soil suspension, for a melted hailstone and for a rain sample. The curves for hail and rain are representative of the 8 samples of hail and of the 10 samples of rain and snow that were tested. In no case was the concentration reduced

Figure 4-4.   Concentrations of freezing nuclei before
and after filtration in rainwater (a), hail (b) and
soil suspension (c).

by more than a factor of ten, at any point in the spectrum, the mean reduction being a factor of four. It can be seen from these data that freezing nuclei found in natural hail, rain and snow and in some soil suspensions, which are active at temperatures between -5 C and -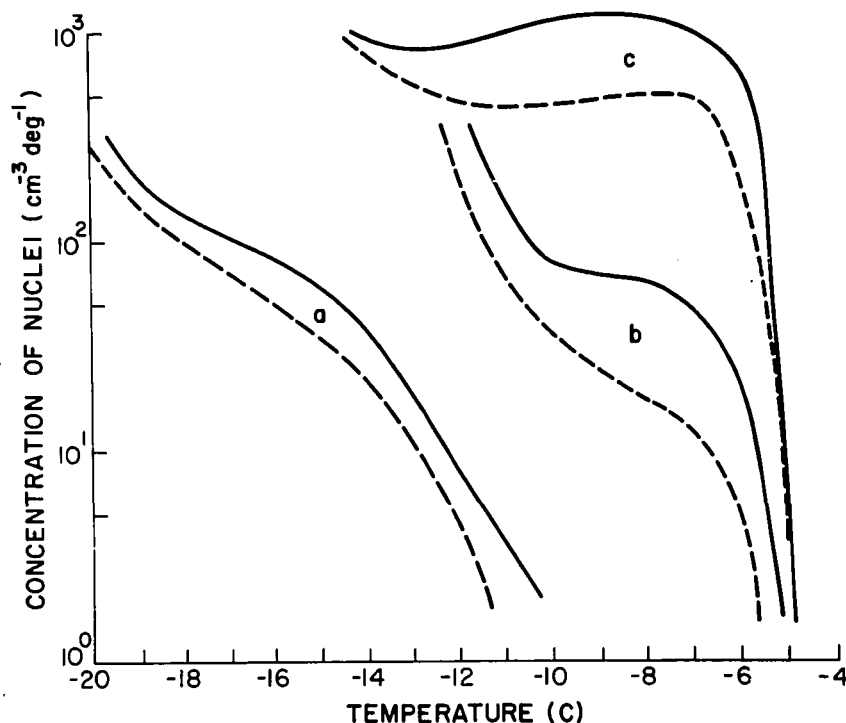20 C, have size distributions such that over 10%, and in some cases 50-80%, of the nuclei are smaller than 0.01 μ and that no major variation exists in this proportion with the temperature of activity.

The acceptability of these results can be supported to some extent by the following argument. Since ice embryos in the supercooled water form on the surfaces of the nucleating particles, the probability of finding a nucleating site on a given particle can be expected to be. proportional to the surface area of the particle.[*] Assuming that such a relation holds for particles down to a diameter of about 0.01 μ and approximating the size distribution of particles in the water with the type of distribution observed for aerosols, the probabilities that nucleation will be initiated in a sample by particles smaller than some chosen value or by those greater than this value can be obtained.

[*] The proportionality of nucleation probability to surface area is likely to hold well for particles which are large compared to the critical size of the ice embryo, but there is no satisfactory way to assess the validity of this relation for particles which are comparable in size to the critical embryo. Estimates for the size of the critical embryo are also uncertain; the calculated values are based on the quasi-thermodynamic theory and bulk values are used for the various parameters. A calculated value for the critical diameter at -5 C is 1.2×10^{-2} μ, and 6×10^{-3} μ at -10 C.

Taking the size distribution of particles to be given (after

Junge, 1963) by the function

$$\frac{dN}{d(\log d)} = c_1 d^{-3} \qquad (1)$$

where N is the concentration of particles with diameters greater

than d, and c_1 is a constant, the distribution of surface areas (S)

will be

$$\frac{dS}{d(\log d)} = c_2 d^{-1} \qquad (2)$$

with c_2 as another constant (assuming all particles to have similar

shapes).

Calculating from this equation the total surface area of particles

between $5 \times 10^{-3} \mu$ and $10^{-2} \mu$ in diameter, and also the total surface

area for particles between $10^{-2} \mu$ and $10^0 \mu$ in diameter, the former is

found to be 1.5 times the latter. Other choices of the limits for the

two size-groups would give different numerical values for the ratio of

surface areas, but the only point that needs to be made here is that

the particles smaller than 0.01μ diameter can probably have as much,

or more, surface available for nucleation as the larger ones. The

measured nucleus spectra show that the ratio of the number of freezing

nuclei below 0.01μ in diameter to the number greater than this size is

from 0.1 to 0.5. Comparing this ratio to the calculated ratio of surface

areas, it appears that, even if the ratio of the areas is revised downward,

or if in fact small particles are less efficient than their surface areas

would indicate, the experimentally determined proportions of small to

large nuclei are not unreasonable.

Vali and Stansbury (1966) have argued that the tendency for most

nucleus spectra to rise exponentially may be taken as an indication that

the probability that a nucleating site active at a given temperature will be found on a particle increases in proportion to the surface area of the particle. Coupled with an exponential distribution of particle sizes (as an approximation to a log-normal distribution), this was thought to lead to an exponentially increasing number of nuclei with decreasing temperature. There is a fallacy in this argument, since the amount of surface area of the particulates which is exposed to the water is the same at all temperatures, and the rise in nucleus concentrations is related to the rise in probability for a nucleating site to be found within that area and not to the sizes of the particles, provided that nucleation occurs on sites that are small compared to the sizes of the particles, as has been maintained to be the case so far. One could give up this latter condition and assume a direct correspondence between particle size and nucleation temperature, in which case the type of argument given by Vali and Stansbury (loc. cit.) may be renewed, but at present the assumption that nucleation takes place on sites that are smaller than the particle sizes appears to be more compatible with the idea that nucleation is a consequence of an interaction at the substrate surface requiring special properties at the nucleating sites. However, until the critical sizes of ice embryos and the actual sizes of nucleating particles become known, this question remains a matter of speculation.

For the problem on hand, estimation of cloud glaciating behaviour, the experimental evidence for the predominance of freezing nuclei less than $0.01\,\mu$ in size is the important conclusion to draw. The unresolved problem of how this comes about does not affect the final results.

2. RELATIVE ABUNDANCE OF FREEZING NUCLEI

In this section the measured concentrations of freezing nuclei are compared with the total particulate content that is generally found in rain and hail. This topic is included here merely as it relates to the question of probability of nucleation by particulates and to their possible identification. The problem of the entry of these particles into the atmospheric precipitation will be taken up in Chapter VI.

The measured concentrations of freezing nuclei, showing the number of nuclei in a sample as a function of temperature, are presented for a variety of samples in the next chapter. Taking values from these data, the concentrations of nuclei active at temperatures warmer than, say, -10 C are: 10 to 100 cm^{-3} in hail and 1 to 10 cm^{-3} in rain or snow. The corresponding value for distilled water is 0.1 cm^{-3}.

In view of the small sizes of many of the freezing nuclei (cf. Section 1), the concentrations of nuclei should be compared to the concentrations of particles of similar sizes, that is, about 0.01 μ. Few published figures are available on this type of measurement. Kumai (1951), examining replicas of snowflakes with an electron microscope, found that in addition to a large (0.1 μ to 10 μ) particle which he thought to be the ice nucleus on which the snowflake grew, and which was present in about 60% of the cases, there were numerous small particles of the sizes of Aitken nuclei (about 10^{-2} μ) present in every case. He estimated the concentration of these to be 10^{12} cm^{-3}.

The only supporting evidence for Kumai's result is in the work of Rosinski (1967) who measured the concentrations of particles 1.5 μ to 100 μ diameter in rain and hail samples. By extrapolating these data,

the concentrations of 0.01μ particles is indicated to be in the range 10^{10} cm^{-3} to 10^{14} cm^{-3} for the various samples. Since these values bracket the value suggested by Kumai, 10^{12} cm^{-3} may be taken as a first estimate for the concentration of particles in precipitation samples. Using this value and taking the concentration of freezing nuclei (at -10 C) in precipitation to be typically 10 cm^{-3}, the fraction of particles that act as freezing nuclei is found to be 10^{-11}. At a temperature of -25 C, this fraction increases to about 10^{-8}. These ratios illustrate the rareness of particles that are capable of effectively promoting the formation of ice embryos. Whether the nuclei are composed of a rare substance or are infrequent configurations of otherwise abundantly-present components is a crucial question for which the answer has not yet been found.

The magnitudes of the figures presented above constitute the main reason why it appears to be futile to attempt the direct identification of the nucleating particles; these nuclei can be distinguished from the inert particles only by actually testing their ability to form ice. Thus, although the presence of a freezing nucleus in a drop of water can be detected with ease, it seems unlikely that the nucleus itself could be found and subjected to testing.

3. REPRODUCIBILITY OF FREEZING TEMPERATURES

As pointed out in Chapter III, the freezing temperature of a drop of impure water is determined by one of the particles in the drop, the particle which can initiate nucleation at the smallest supercooling. The freezing temperature of a drop can therefore be equated to the characteristic temperature or temperature of activity of a nucleus. This section describes experiments which were performed to determine whether these characteristic temperatures are permanent or readily altered properties of the nucleating particles.

The reproducibility of the freezing temperatures of individual drops has been examined by freezing, melting and then refreezing sets of drops on the cold stage. Figure 4-5 shows the correlation between the first and second freezing temperatures of 144 drops. The average freezing temperature of the 144 drops was 0.02 deg warmer in the second run than in the first. The average change in freezing temperature (irrespective of direction) was 0.6 deg, and the freezing temperatures of 90% of the drops changed by less than ± 1.6 deg. This result is typical of the results of a number of such experiments.

The first question raised by these observations is whether two freezing temperatures of a drop in successive runs are due to the actions of the same nucleus or of two different nuclei. To answer this question, it may be recalled from the definitions given in Chapter III that the probability of finding a nucleus active between temperatures θ and $\theta + \Delta\theta$ in a drop of volume V is given by the nucleus spectrum as $V \cdot k(\theta) \cdot \Delta\theta$. This probability is independent of the presence of other nuclei and is therefore equal to the probability that a drop
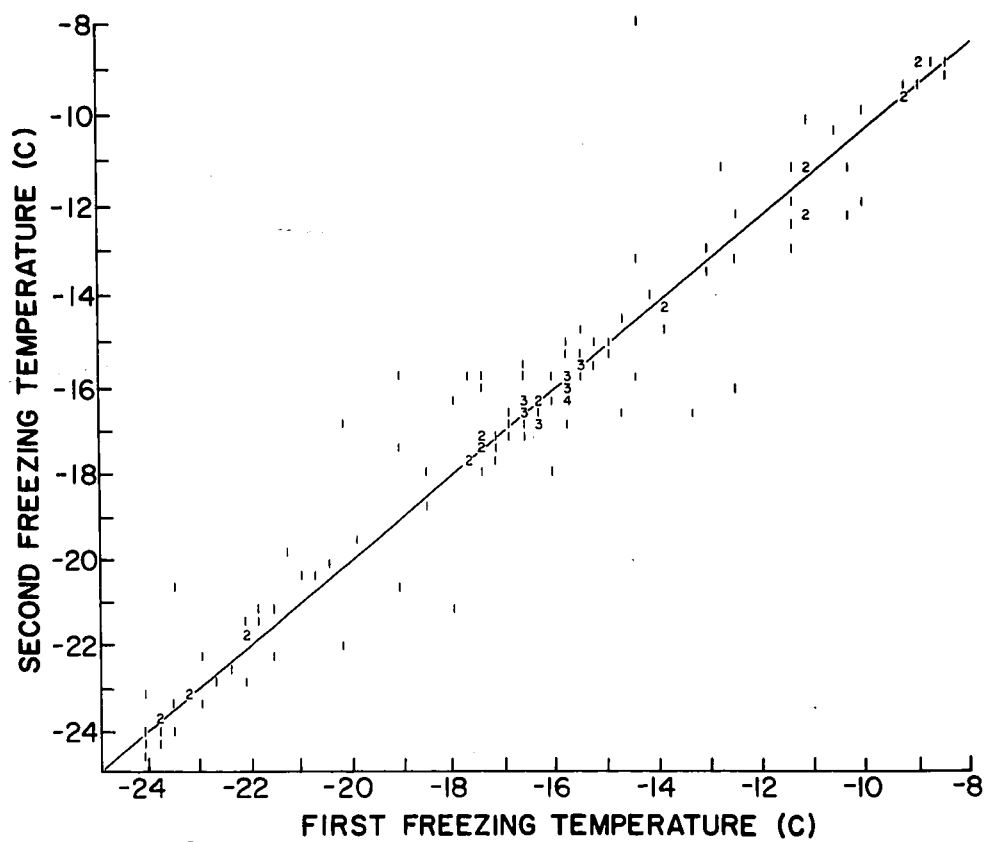
Figure 4-5.   Correlation between first and second
freezing temperatures of 144 drops.

originally freezing at θ and then at $\theta + \Delta\theta$ may have been nucleated

by two different nuclei on the two occasions. The probability for

two competing nuclei to be present within a temperature interval of

1.6 deg for the nucleus spectrum of the sample used is thus found to

be 0.1 at -10 C, 0.5 at -22 C and 0.9 at -23 C. For temperatures

warmer than -23 C, it is therefore likely that the observed changes

in freezing temperatures of drops reflect changes in the temperature

of activity of the nucleating particle, and not the alternate actions

of two nuclei. The facts that the freezing temperatures change in

both directions with about the same frequencies at warm and at cold

temperatures, and that the magnitudes of the changes are approximately

the same in all temperature regions, point to this same conclusion.

One can therefore look upon the changes shown in Fig. 4-5 as changes

in the activities of nuclei, for all except the coldest temperatures;

the results indicate that the temperatures of activity of individual

nuclei are remarkably constant in comparison with the differences

between the temperatures of activity of various nuclei.

With several cycles of freezing and melting of drops, interesting

patterns emerge for the changes in freezing temperatures. Figure 4-6

presents typical results obtained in experiments in which 30 to 60

cycles of freezing and melting were carried out. It is seen from

this figure that some drops have very reproducible freezing tempera-

tures, some show abrupt changes, and some change their freezing tem-

peratures irregularly. The changes in the average freezing temperature

of 144 drops are also shown in Fig. 4-6, demonstrating that the changes

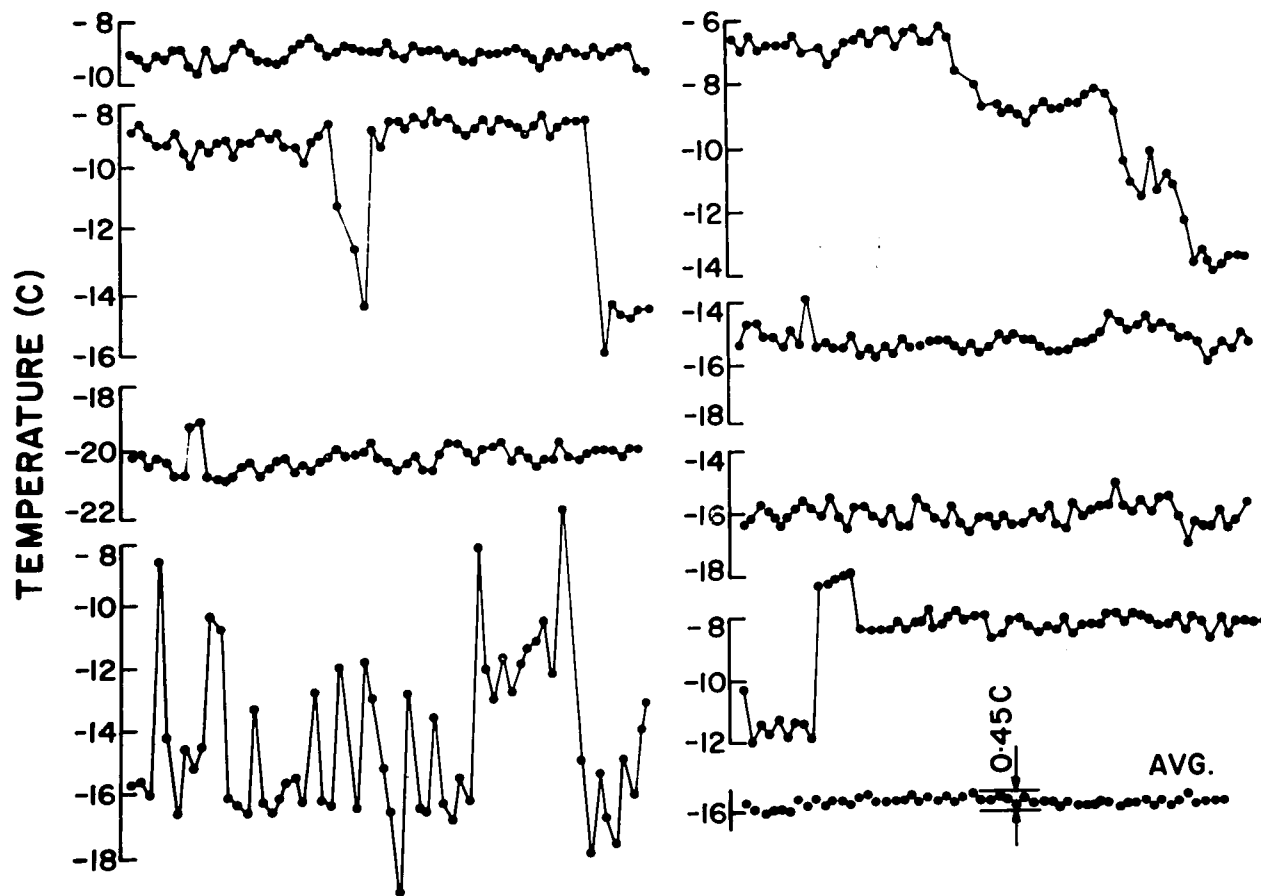in the freezing temperatures of individual drops tend to cancel, and

Figure 4-6.   Fluctuations in freezing temperatures
of drops on repeated freezings.

that no systematic shift of freezing temperatures occurs. In these data there appears to be no systematic grouping in the types of changes that occur for drops freezing at warm or at cold temperatures, but this aspect needs further analysis. Some variations of the freezing temperatures must result from the statistical nature of the nucleation process even for unchanged nuclei, and it may be thought that the freezing temperatures of drops which show the least degree of fluctuation reflect this effect.

Refreezing experiments with samples filtered through $0.01\,\mu$ filters gave similar results to the experiments using unfiltered samples. Ninety percent of the changes in freezing temperatures fell within intervals of ±1.2 C to ±1.7 C for the various samples. Nuclei less than $0.01\,\mu$ diameter are thus found to retain their activity to the same extent as larger nuclei.

By introducing a 16-hour period between first and second freezings, during which time the drops were left on the cold stage under a loosely-fitting cover and kept at $+20$ C, the deviations between freezing temperatures increased somewhat so that 85% of the changes were less than ±1.6 C and the 90% range increased to $+2.6$ C (warmer) and -1.7 C (colder). The average freezing temperatures of the two runs differ by 0.1 deg. The increase is slight and is caused mainly by a rise in the freezing temperatures of a few drops which originally froze at temperatures below -22 C.

The effects of drying of the nuclei and of exposure to air have been studied in the following manner: After the first freezing, the drops were evaporated under reduced pressure. The residues left by the drops on the supporting surface were then allowed to come in contact with air for various periods of time. The supporting plate and the residues were

at room temperature during these intervals. After placing drops of

distilled water over each residue, a second freezing experiment was

carried out. The results of these experiments are summarized in

the table below:

PERIOD OF EXPOSURE TO AIR	CHANGE IN AVG. FREEZING TEMPERATURE	PERCENT OF CHANGES LESS THAN ± 1.6 C	90% RANGE
3 hr	-0.3 C	79%	$\begin{cases} +2.1 \text{ C} \\ -2.9 \text{ C} \end{cases}$
18 hr	+0.1 C	85%	± 1.9 C
4 day	-1.3 C	52%	$\begin{cases} +2.0 \text{ C} \\ -4.5 \text{ C} \end{cases}$

These data indicate that there is some loss of activity with time.

Although the 3-hour and 18-hour experiments do not show progressively

increasing effects, the 4-day delay is the only case of major change

observed. In that experiment, equal reductions in freezing temperatures

occurred at all temperatures. From the works of Birstein (1960) and

Georgii (1963), it is known that deactivation of nuclei can be caused

by adsorbed gases, and the possibility that some contamination occurred

in our experiments cannot be excluded.

The aging characteristics of individual nuclei are observed in

the drop refreezing experiments. The extension of these experiments

to periods longer than a few days was impractical, and therefore the

overall changes in nucleus content after long periods of storage were

studied instead. The nucleus content of samples which were kept frozen

was found to remain unchanged even after years of storage in closed

containers at -20 C. On the other hand, the nucleus content of

samples of liquid water diminishes with time. This effect has already

been noted by Stansbury and Vali (1965).

Figure 4-7 shows two spectra for a sample of melted hail, one

obtained immediately following melting, and the other after a period

of six weeks, during which time the sample was at temperatures between

20 C and 25 C. This example shows the most severe case of aging that

was observed for comparable periods. In other samples the reductions

in nucleus concentration were about a factor 2 to 4, with most of the

change occurring within the first week. Figure 4-8 shows nucleus

spectra for two portions of a sample of rain after 10 weeks of storage,

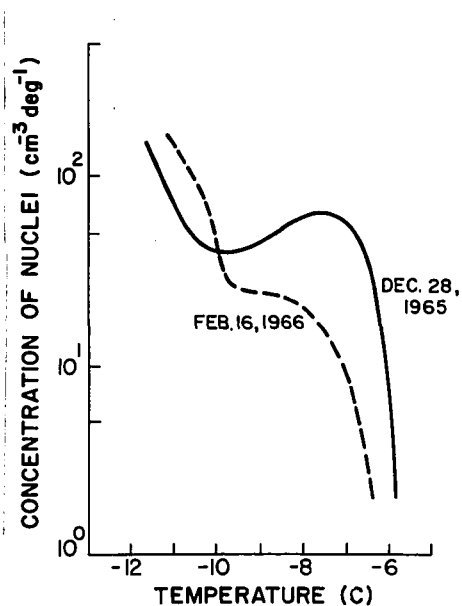one part having been stored frozen, the other at room temperature.

Figure 4-7. Nucleus spectra for sample of hail before
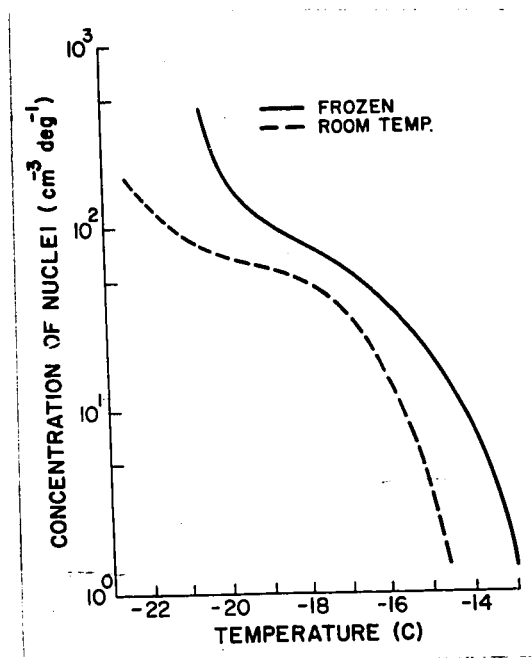and after 6 weeks' storage at room temperature.

Figure 4-8.   Nucleus spectra for portions of sample of
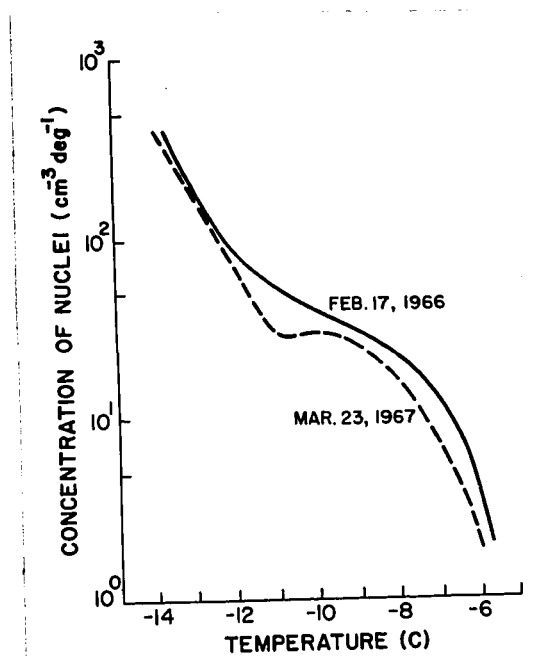rain after 10 weeks' storage at temperatures below 0 C
and at 20 C.

Figure 4-9.   Nucleus spectra for sample of hail before
and after 5 weeks' storage at 5 C.

The changes in nucleus concentrations after 5 weeks of storage at 5 C are shown for a sample of hail in Fig. 4-9. The maximum reduction in nucleus concentration is a factor of 2 (at -11 C), and the average reduction is about a factor of 1.5.

From the foregoing, it appears that the nucleus concentrations of water samples are reduced when stored for long periods of time, and that the rate of reduction increases with increasing temperatures of storage. The dependence of the rate of loss of nuclei on temperature indicates that the effect is due mainly to changes in the nucleating abilities of particles, rather than to sedimentation, as the rate of sedimentation does not depend appreciably on temperature. The increase found in Fig. 4-7 for the concentrations of nuclei at colder temperatures also supports this conclusion. In any case, the changes in nucleus concentrations are small; the corresponding average reductions in nucleating temperatures are about 1 deg for samples stored at room temperatures and about 0.5 deg for samples stored at 5 C (after 5 weeks).

It is evident from these results that for the majority of freezing nuclei the ability to nucleate ice is a permanent property of the nucleating particle. The temperature at which nucleation occurs is defined by the characteristics of the nucleus, and its nucleating ability is little affected by long periods of exposure to air or by repeated nucleation. Some alterations of nucleating ability are observed and occasionally the changes are large; further exploration of these effects is required and could lead to better understanding of the nucleation process and of the nature of the nucleating particles. One may also

conclude that the freezing characteristics observed in the laboratory can be used to describe the action of freezing nuclei in the atmosphere unless additional influences not present in the experiments (such as radiation, electric fields, adsorbed contaminants) are found to be of major importance.

4. SOURCES OF FREEZING NUCLEI

Since soils are among the most important sources of atmospheric particulates, the effectiveness of soils as ice nuclei has been extensively investigated (see summaries by Bigg, 1961; Mossop, 1963; and Dufour, 1966), however mostly by means of cloud chambers and by testing the mineral components of soils only. Because our technique of measurement of nucleating activity is different, and because it was thought desirable to test soils in their natural form, a number of soils were examined on a comparative basis.

The soils were used in the form in which they were collected from the field,[*] with no special treatment except for light crushing of large agglomerates. Each sample was prepared for testing by adding 0.02 g of soil to 40 g of distilled water. Freezing experiments were conducted with each sample within a few hours after the preparation of the samples, but some sedimentation usually occurred even during this time. Since the size distributions of particles in the samples were not known and were evidently quite varied from sample to sample, the extent of sedimentation is just one aspect of differences in characteristics. Uniformity of procedures was maintained, however, ensuring comparability of the results.

Figure 4-10 shows a number of nucleus spectra that were obtained for samples of surface soils. The origins of the temperature scales are displaced for each spectrum in order to separate the curves, and the temperatures are given at which the nucleus concentrations reach

[*]The samples were obtained from the Department of Soil Science, Macdonald College of McGill University.
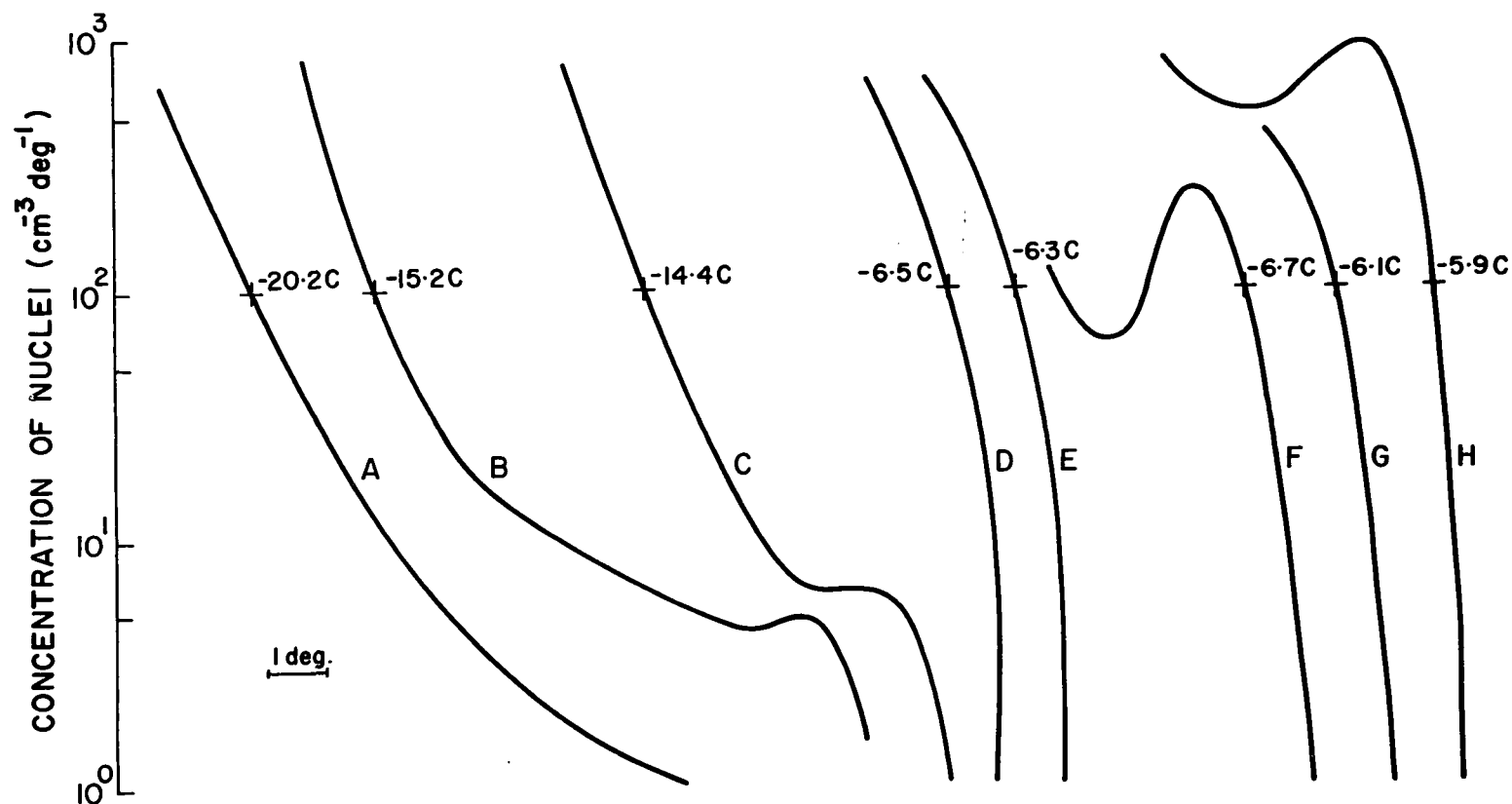
Figure 4-10. Concentrations of freezing nuclei in 0.05% suspensions of surface soils.

A - Volcanic ash, St.Lucia
B - Clay soil, Quebec
C - Clay soil, Quebec
D - Humus soil, Alberta

E - Humus soil, Quebec
F - Loam soil, Quebec
G - Loam soil, Saskatchewan
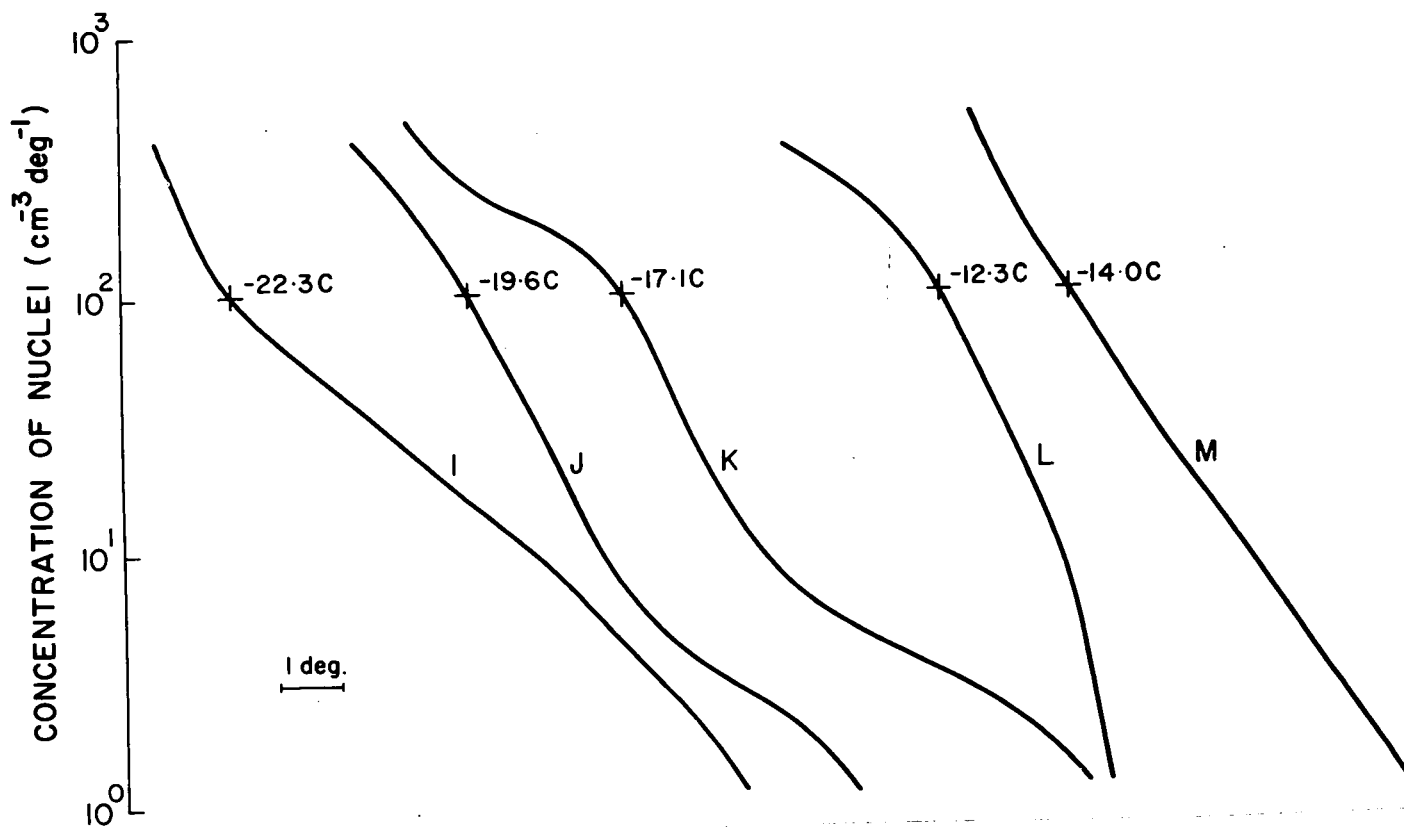H - Peat soil, Quebec

Figure 4-11. Concentrations of freezing nuclei in 0.05% suspensions of clay minerals.

I - Kaolinite, Georgia A.P.I. No. 2   L - Bentonite, Wyoming
J - Montmorillonite,   M - Bentonite, Alberta
        Mississippi, A.P.I. No.22
K - Illite, Illinois, A.P.I.No.35

$100 \text{ cm}^{-3} \text{ deg}^{-1}$. In Fig. 4-11, nucleus spectra for samples of pure

clays are presented in a similar manner. It is immediately evident

from a comparison of these two figures that the surface soils contain

more nuclei active at warm temperatures than the clay samples.

Especially remarkable are the high concentrations of nuclei active near

-5 C in samples D to H in Fig. 4-10. The main difference between the

pure clay and the surface soil samples is that the surface soils in

general contain a variety of different substances in addition to the

basic clay particles that make up the soil. The highest nucleus con-

centration at -5 C was given by a sample of peat soil (H in Fig. 4-10)

which had the highest content of organic matter among the samples tested;

it is possible that nucleus content and organic components of soils are

related.

Experiments have also been performed with two pairs of samples,

each pair of which originated from the same location but from two different

depths below the surface. The nucleus spectra obtained for one of these

pairs is shown in Fig. 4-12. Also shown in this figure are the spectra

obtained for these samples after filtration with 0.01μ pore-size filters.

The other pair of samples gave closely similar results. The nucleus

contents of the surface samples were in both cases higher than the samples

from greater depth. This result tends to confirm the indication given by

Figs. 4-10 and 4-11 that the most active nuclei in the samples were asso-

ciated with substances found mainly in the surface layers of soils.

The difference in nucleating ability between surface and sub-surface

soils is in the wrong direction to be explained on the basis of particle

sizes. Clays are generally composed of particles between 0.1 μ and

1 μ in diameter, whereas the surface soils are mainly of larger aggre-

gates (1-10 μ). Visibly stronger sedimentation was observed, in the

samples of surface soils.
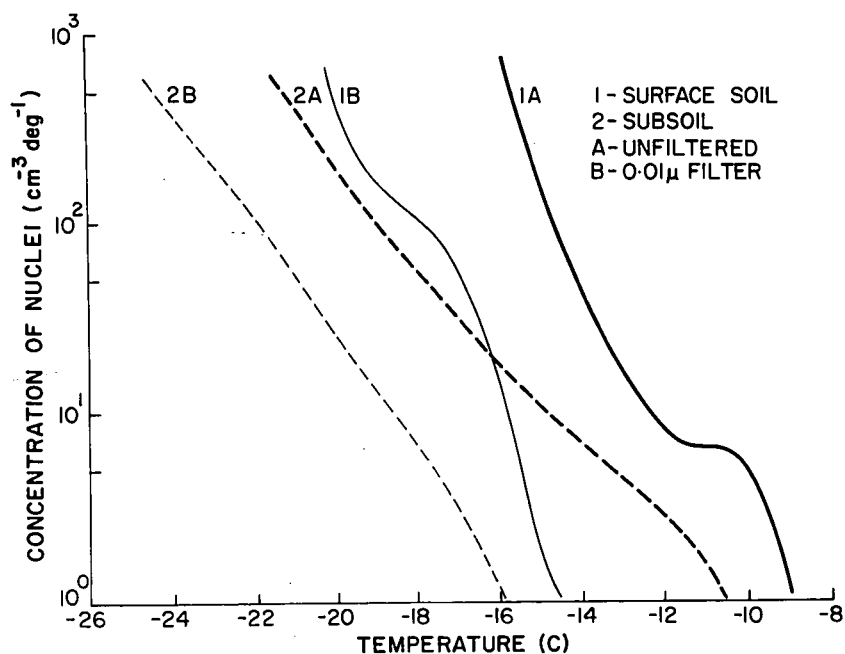
Figure 4-12. Nucleus spectra for surface and sub-surface
soil samples from same location.

Filtration experiments revealed that for the nuclei active near

-5 C the proportions of nuclei less than 0.01 μ in diameter were higher

than for the nuclei active at temperatures of -10 C or lower. Figure

4-13 shows the nucleus spectra obtained for the sample of peat soil

(curve H in Fig. 4-10) without filtration and after filtration with a

0.01 μ pore filter. The reduction in nucleus concentrations resulting

from the removal of particles larger than 0.01 μ is very small for

temperatures above -8 C, a factor of 2 approximately, but increases

to a factor of 20 at temperatures near -16 C. Figure 4-13 is typical
of the results that were obtained with the five samples which exhibited
high nucleus concentration at temperatures close to -5 C (samples D, E,
F, G and H in Fig. 4-10). Examples for the reductions in nucleus
concentrations that result from the filtering (with 0.01 μ pore size
filters) of surface soils which do not have high nucleus concentrations
at warm temperatures are shown in Fig. 4-12. The reduction factors in
this case vary from 50 to 100; in other similar samples the reduction
factors were from 10 to over 100.

After filtration of the suspensions of clays I, J, K, L and M, the
nucleus concentrations of these samples did not exceed the concentrations
of nuclei in the distilled water. This is in agreement with the generally
applicable particle sizes for clays, and indicates that no appreciable
amounts of very small particles of clay, or of other substances, capable
of promoting nucleation at temperatures warmer than -20 C were present.

The experimental results described in this section differ from
results on the nucleating ability of soils that were reported by
Pruppacher and Sänger (1955), by Mason and Maybank (1958), and by
Paterson and Spillane (1967), principally in that warmer nucleation
temperatures were found in our experiments. These authors reported
"threshold temperatures" of -12 C for most minerals and -7 C for only
one sample. The small sizes of the nuclei, which we have found to prevail,
contrasts with the sizes (0.1 μ or larger) that they reported to be
required for nucleating particles. Schulz (1948) and Nagy (1966) have
reported nucleation in suspensions of sand, calcite, barytine and mica
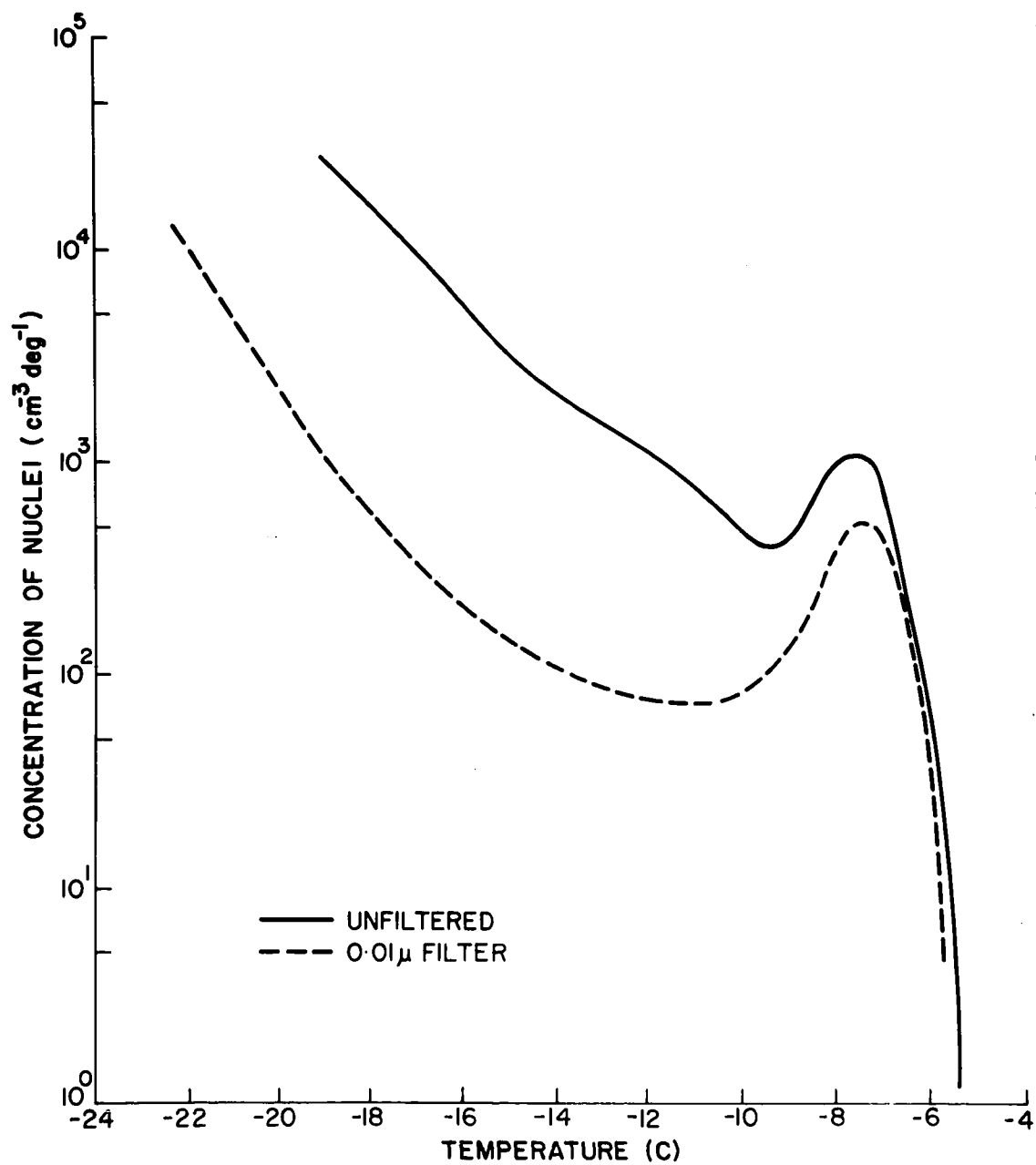at temperatures of -3 C to -5 C, but these experiments utilized millimeter-

Figure 4-13.   Concentrations of freezing nuclei in 0.05%
suspension of peat soil, with and without filtration
through filters of 0.01 μ pore size.

sized particles. No detailed explanation can be given for these disparate findings, because of differences in experimental techniques and conditions, and because of variations in the substances tested. In general, one can point to the fact that in our experiments composite soils were used, whereas previous work was mainly done with the mineral components of soils only.

In summary, the most significant finding of these experiments is that five out of the eight samples of surface soils tested were found to contain high concentrations of freezing nuclei active at temperatures close to -5 C, and that these nuclei are smaller than 0.01μ in diameter. Since clay samples were found not to contain such active nuclei, and the proportions of nuclei less than 0.01μ size were found to be small in these samples, the most active nuclei in the surface soil samples appear to be associated with some minor (perhaps organic) component of these soils.

For the freezing nucleus content of the atmosphere the activity and the small sizes of the nuclei in surface soils are likely to be of major importance. Similarities between soil suspensions and precipitation samples, with respect to the rapidly rising nucleus concentrations at temperatures between -5 C and -6 C, and with respect to the high pro-portions of small nuclei, strongly suggest that the freezing nuclei active at temperatures above -10 C in precipitation samples are of soil origin. The most active nuclei were found in the types of surface soils which under dry conditions are subject to strong wind erosion and are fairly common to most areas. These soils are therefore very likely to be among the major sources of atmospheric ice nuclei. The transport and collection mechanisms that can provide for the entry of particles of soil origin into the precipitation are discussed in Chapter VI.

V.   FREEZING NUCLEUS CONTENT OF PRECIPITATION

Research on atmospheric ice nuclei has been based chiefly on measurements of the nucleus content of air. These measurements rely on the activation of the airborne nuclei by some manner of humidification and cooling. Comparatively little attention has been paid to the nucleus content of natural precipitation, although such measurements would be more direct indicators of conditions within the. clouds.

Soulage (1957) devised a method to reactivate the residues of evaporated snow crystals. However, only about 1 out of 10 crystals could be re-formed at -21 C, even though the original crystals were formed at temperatures between -12 C and -19 C. Hoffer and Braham (1962) captured frozen cloud droplets from an aircraft, melted them and observed the temperatures at which the droplets froze when cooled again. They found the mean freezing temperatures of the drops to be -25 C for drops of 100 μ diameter and -22 C for drops of 500 μ diameter. Since the coldest temperatures in the clouds in which the collections were made were warmer than -15 C, they concluded that the freezing of the droplets in the cloud did not result from the action of nuclei within them.

Measurements on the nucleus content of precipitation have been under way at McGill University since 1959. Nucleus content is determined from observations of the freezing temperatures of drops of rain, hail and snow. The results of these measurements have been reported by Barklie and Gokhale (1959), Barklie (1960), Stansbury (1961), Vali (1964), Stansbury and Vali (1965), Schlien (1967) and Bishop (1968).

The most important findings of these experiments, based on the analysis
of about 100 samples of precipitation, are:

(i)   The nucleus content of hail samples is higher than

      that of rain and snow (Barklie, 1960; Schlien, 1967).

(ii) Hail from western Canada has higher concentrations of

      nuclei than hail from eastern Canada (Stansbury and

      Vali, 1965; Schlien, 1967).

(iii) There is no major variation in the nucleus content of rain

      and snow with geographical origin. Samples obtained from

      13 stations across Canada have shown no systematic differ-

      ences (Schlien, 1967).

Collection of the samples is one of the major problems in work
with natural precipitation. The need for collection methods that do
not influence the samples, and the unpredictability of times and loca-
tions of precipitation (especially for hail) lead to contradictory
requirements for the collection methods. In addition, since no inde-
pendent evaluations of nucleus content have been available for comparison,
it has been difficult to assess the reliability of the results.

The data presented in this chapter have been obtained in order to
augment the observations of the previous series of experiments, and to
establish the reliability of the collection techniques.

Figures 5-1 and 5-2 present the nucleus spectra for hail samples
collected in 1965 and in 1967 respectively. The ranges in which the
majority of the spectra lie and the spectra for a few samples of
exceptionally high or low nucleus content are shown. The individual
spectra are shown in Figs. 5-3 and 5-4. All samples except one (65-A)
originate from the southwestern part of Alberta.
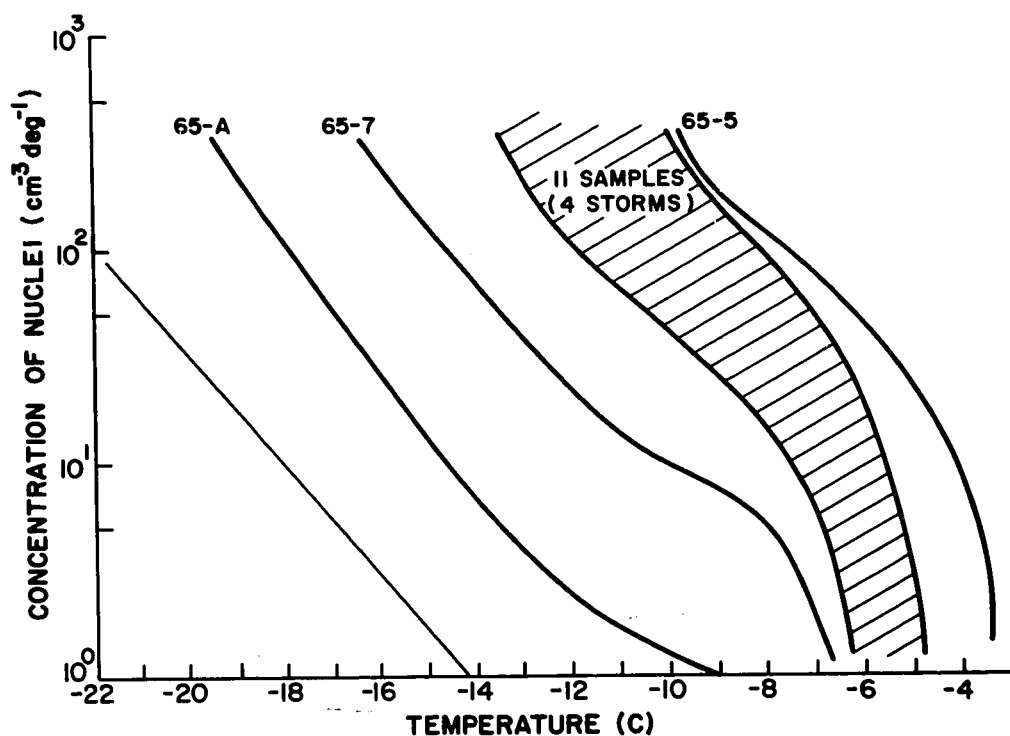
Figure 5-1. Range of nucleus concentrations for hail
samples collected in 1965 in Alberta and in Ontario
(sample 65-A). The thin line indicates nucleus content
of distilled water for comparison.
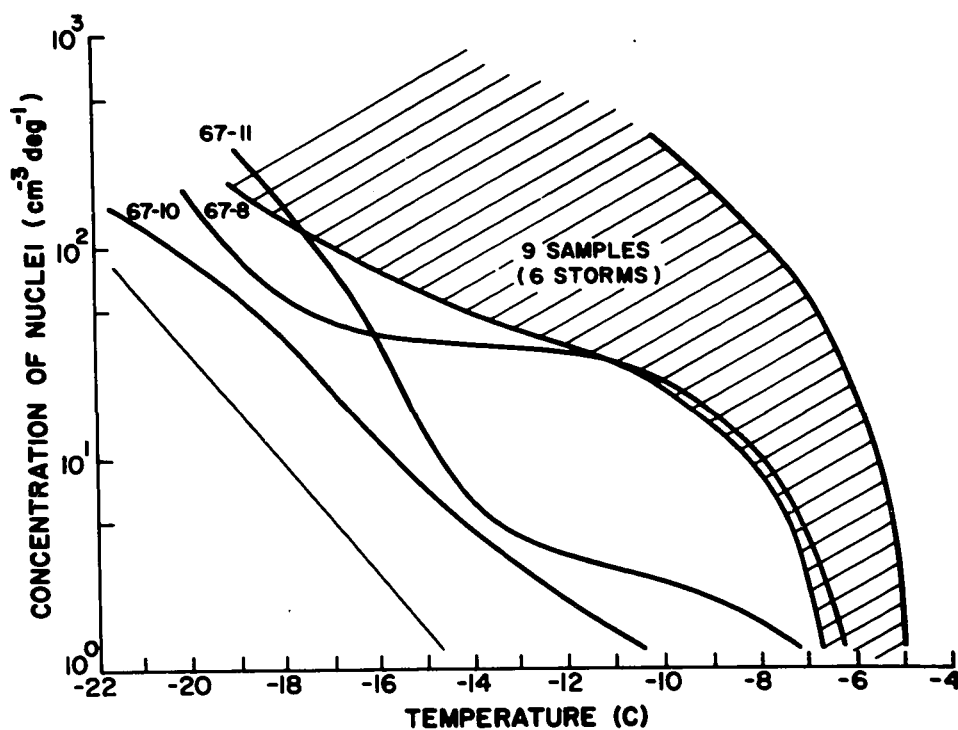

Figure 5-2. Range of nucleus concentrations for hail
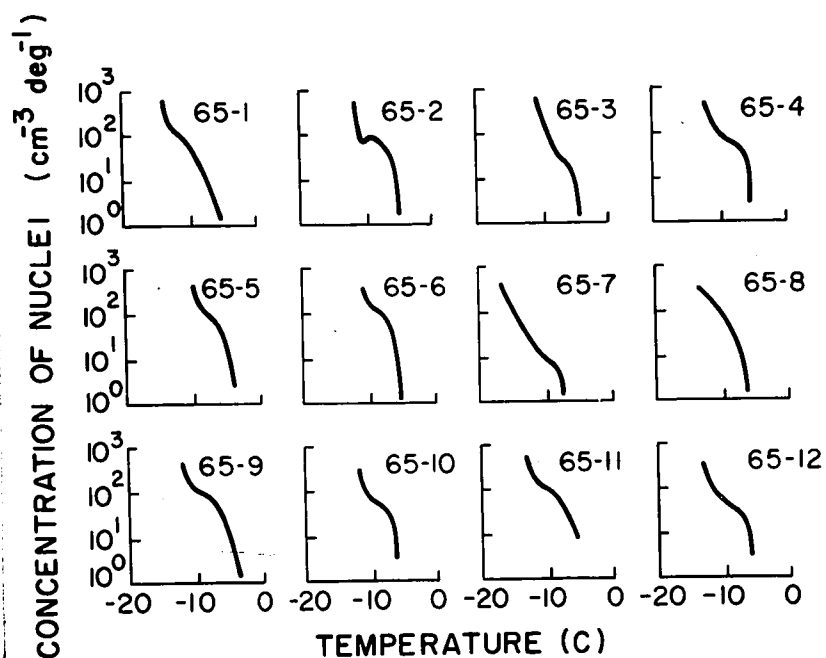samples collected in Alberta, summer of 1967.

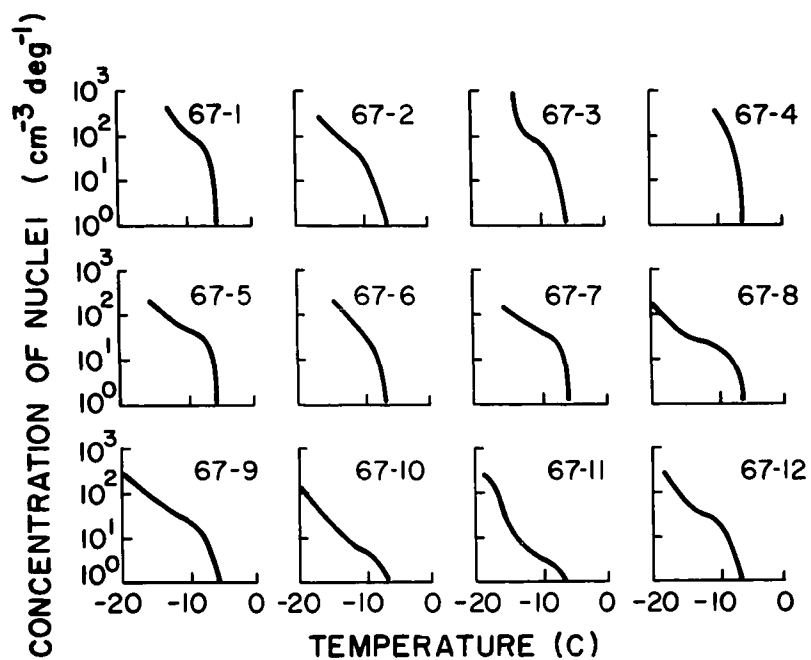Figure 5-3. Individual nucleus spectra for hail collected in 1965. These are summarized in Fig. 5-1.

Figure 5-4. Individual nucleus spectra for hail collected in 1967. These are summarized in Fig. 5-2.

The concentration of nuclei in sample 65-A from southeastern Ontario
is lower than in the majority of samples from Alberta, in agreement
with previous findings. In 1965 the hailstones were all obtained
from volunteer collectors who collected the hailstones from the ground
after the storms. In 1967 the samples were collected in plastic-lined
baskets. Some of these samples were obtained from a network of farmer-
operated stations, but most were collected by the crew of a mobile
sampling unit. The network collectors were kept covered and the covers
were removed just before or during the passage of the storm, the mobile
collectors were assembled just before use with new liners. Each liner
was used only once. There appears to be some tendency for the 1967
samples to have lower concentrations of nuclei, but the difference is
not a major one. Sharp increases in concentration with decreasing
temperature appear in the spectra at about -6 C for samples from both
years.

The concentrations of freezing nuclei in 40 samples of rain
collected from intense showers during the summer months in Alberta
were found to lie within the range indicated by the solid lines in
Fig. 5-5. The spectra for 23 samples collected by the mobile unit are
distributed fairly uniformly within the whole band shown in this figure,
while spectra for the 17 samples obtained from the farmer network fall
within the narrower range indicated by broken lines. All collections
were made with identical equipment, small bags with plastic funnels
which were uncovered only after the onset of rain, but differences in
handling could have occurred. The fact that the less well controlled
collections by farmers yielded samples comparable to the samples obtained
by trained personnel is a reassuring indication of the realibility of
sampling.
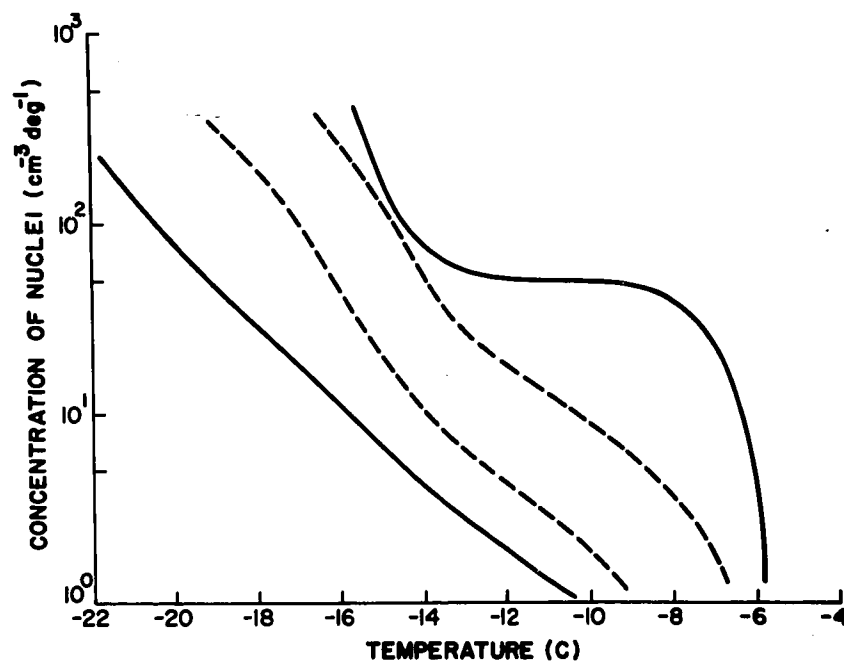
Figure 5-5.   Range of nucleus concentrations in 40
    samples of rain from Alberta, summer 1967.

On the whole, the concentrations of nuclei in hail appear to
be higher than in rain.   In Fig. 5-6 the ranges of concentrations
for 9 samples of hail and 40 samples of rain are replotted from
Figs. 5-2 and 5-5.   All these samples originated from the same season
and geographical area, but not from the same storms.
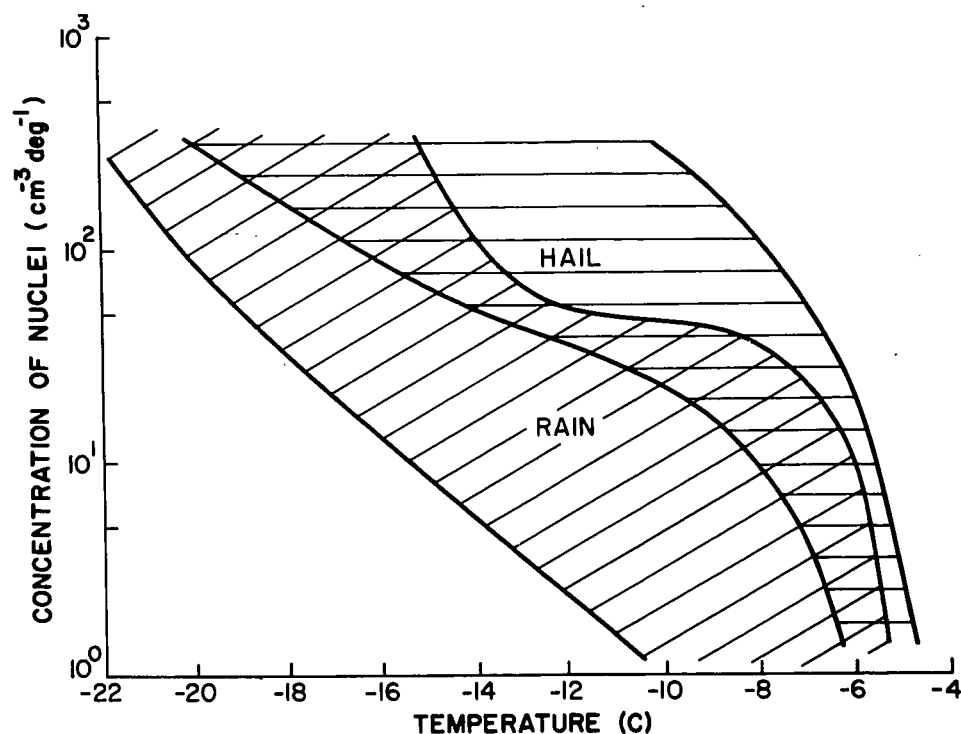
Figure 5-6.   Ranges of nucleus concentrations in hail
and in rain from Alberta (summer of 1967).

From three storms in 1967, samples of both rain and hail have
been collected.   Spectra for 2 samples of rain and 4 samples of hail
from one of these storms are shown in Fig. 5-7.   Hail samples 1, 2
and 3, as well as both rain samples, were taken from the drain of a
6' x 15' plastic-coated tray (on top of a truck).   Sample B is from
a plastic-lined basket set out about 100' away from the tray collector,
and had some rain mixed with the hail.   The numbering of the samples in
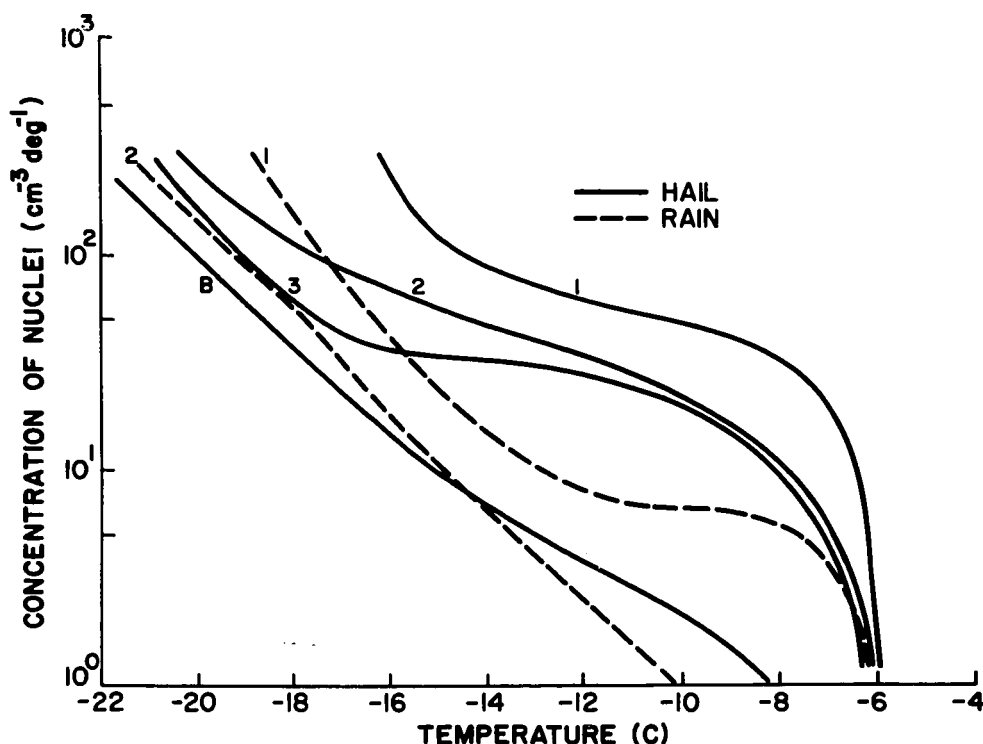
Figure 5-7. Nucleus spectra for sequences of four
hail samples and two rain samples collected on August
6, 1967 from same storm.

the figure indicates the order in which they were collected; the

relative timing of the rain and hail samples is not known. At the

sampling location, the storm lasted 12 minutes. The average rain

intensity during this time was about 50 mm hr^{-1} and the maximum record-

ed rate was 130 mm hr^{-1}. The hailstones were about 0.5 cm diameter.

The higher nucleus content of hail samples 1, 2 and 3, compared to the

rain, is quite evident from this figure, and it is most unlikely that

this difference would have resulted from the manner of collection. The

lower nucleus content of sample B may indicate that some contamination

from the collecting tray was occurring, but one would expect rain to

be affected more seriously by such contamination than hail. The other

two pairs of samples showed similar differences. The nucleus content

of hail thus appears to be higher than that of rain, even if both

originate from the same storm.

Eleven of the forty rain samples (cf. Fig. 5-5) originated from
storms which produced hail within an area of 3 mi radius around the
collection point and with the duration of hailfall at least partially
overlapping the duration of rain collection. No grouping of these
samples within the general range is evident, as shown in Fig. 5-8.
This finding also points to an association of high nucleus concentra-
tions with hail specifically and not with the storm as a whole, which
means either that hail develops whenever the air entering the storm
has high concentrations of nuclei active at warm temperatures, or that
differences in the growth processes of rain and of hail lead to different
proportions of nuclei to water mass in hail and in rain.
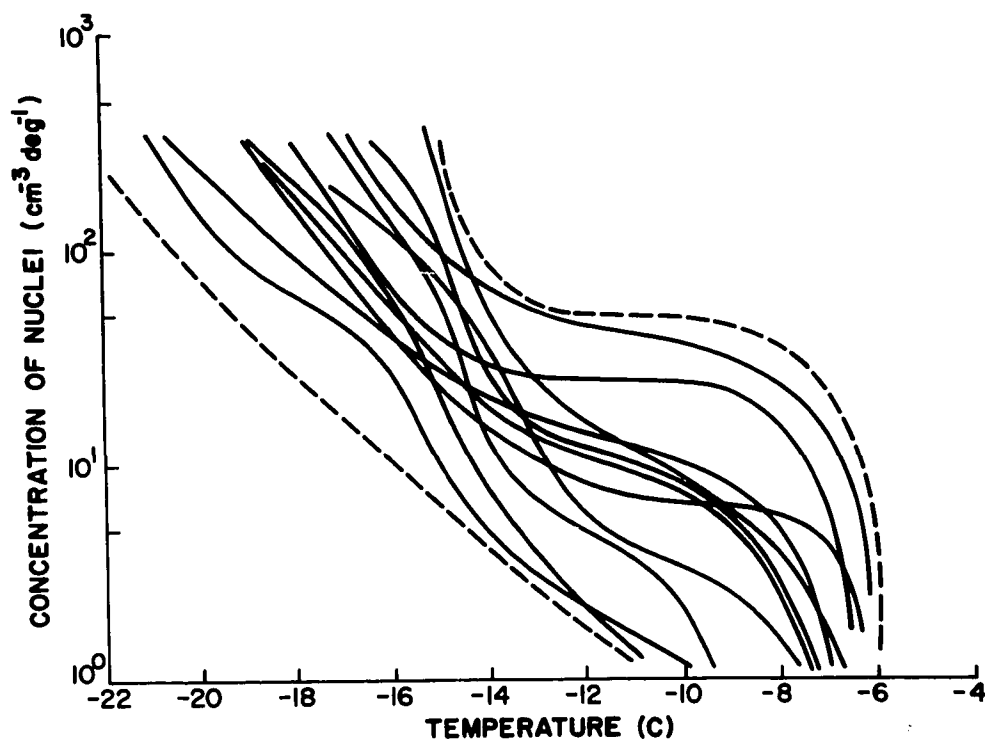
Figure 5-8. Nucleus spectra for 11 rain samples from
hailstorms (full lines). Broken lines indicate range
of concentrations for 40 samples collected from all
storms.
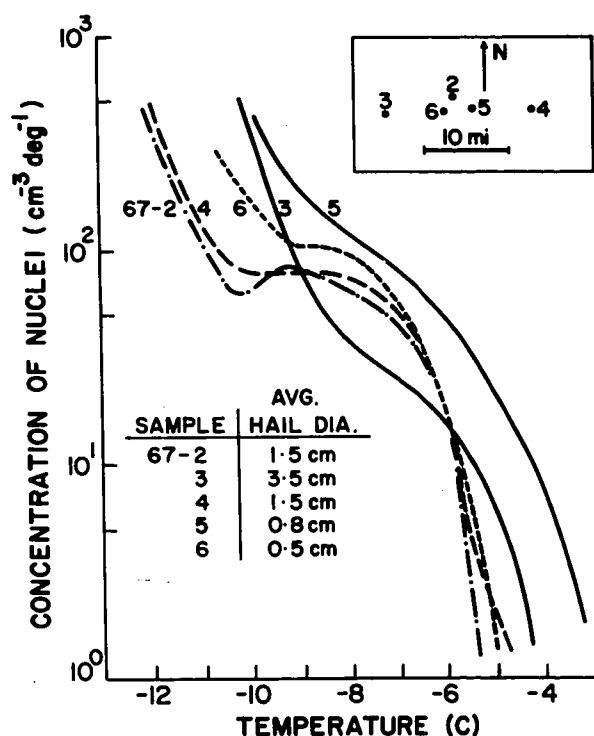
Figure 5-9. Nucleus spectra for five samples of hail
from storm of August 27, 1965. Relative positions of
collection points and average hail sizes are shown by
insets.

Two cases in each of which samples of hail were obtained from five

different locations along the storm swath were available for analysis.

Spectra obtained for one of these cases are shown in Fig. 5-9. The

results for the other occasion have been reported by Schlien (1967)

and are very similar to those shown here. All samples for these sets

were collected from the ground by farmers. As shown by Fig. 5-7, the

maximum variation in concentration is about a factor of ten, and the

differences in temperatures at fixed concentrations are about three

degrees. The maximum differences among samples in general (Figs. 5-1

and 5-2) are considerably larger than this.

Simultaneously collected pairs of rain samples from the same locations were obtained in 9 cases. These collections were planned to provide a measure of the consistency of the collection technique. Figure 5-10 shows the spectra for 3 representative pairs of these samples, indicating that although variations of up to factors of four occur, the differences between the simultaneous samples are smaller than the differences between samples from separate occasions. It thus appears that the nucleus spectra for the rain samples reflect the properties of the samples, but that there is a minor influence from the collectors. Bishop (1968) found that with large plastic bags used for collection, the variation between the nucleus concentrations of simultaneously collected samples is less than a factor of 1.5. This collection technique has the advantage that no part of the collecting device is used more than once.
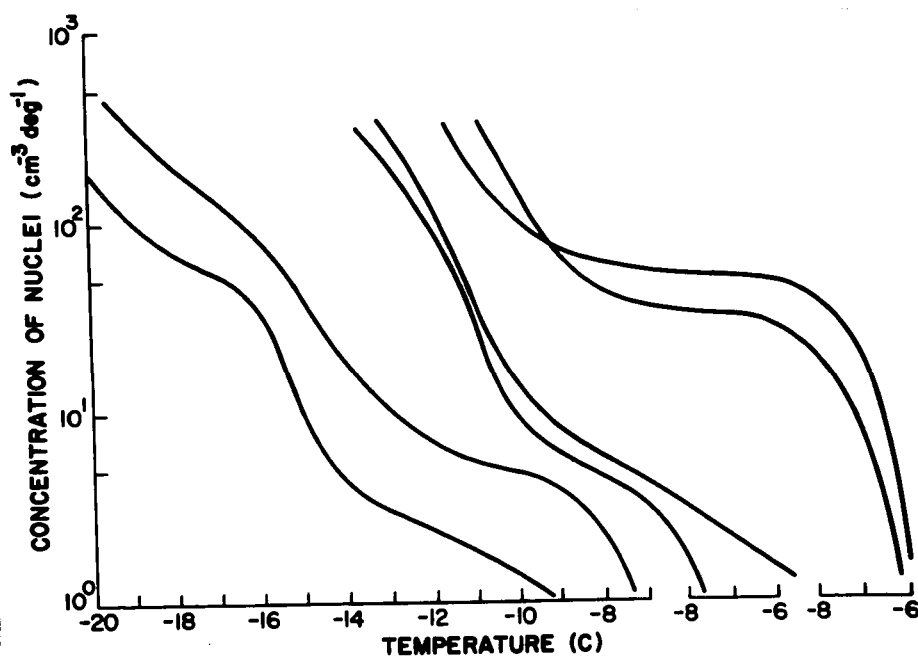
Figure 5-10. Nucleus spectra for three pairs of rain samples. Pairs collected simultaneously with duplicate equipment.

Samples of rain from convective type storms were also collected at two stations in the Montreal area. Each location lies about 15 miles from the center of the city and is outside the area of severe air pollution. Some of the collections were made by the use of funnels and some by large plastic bags. The range covered by the nucleus spectra of 7 samples of summer rain is shown in Fig. 5-11. No difference is evident in these spectra between samples collected by the two different methods. Also shown in Fig. 5-11 is the range of the nucleus spectra for the rain samples from Alberta. The higher nucleus content of precipitation in Alberta is evident from this diagram. This is in accord with the difference found for hail.
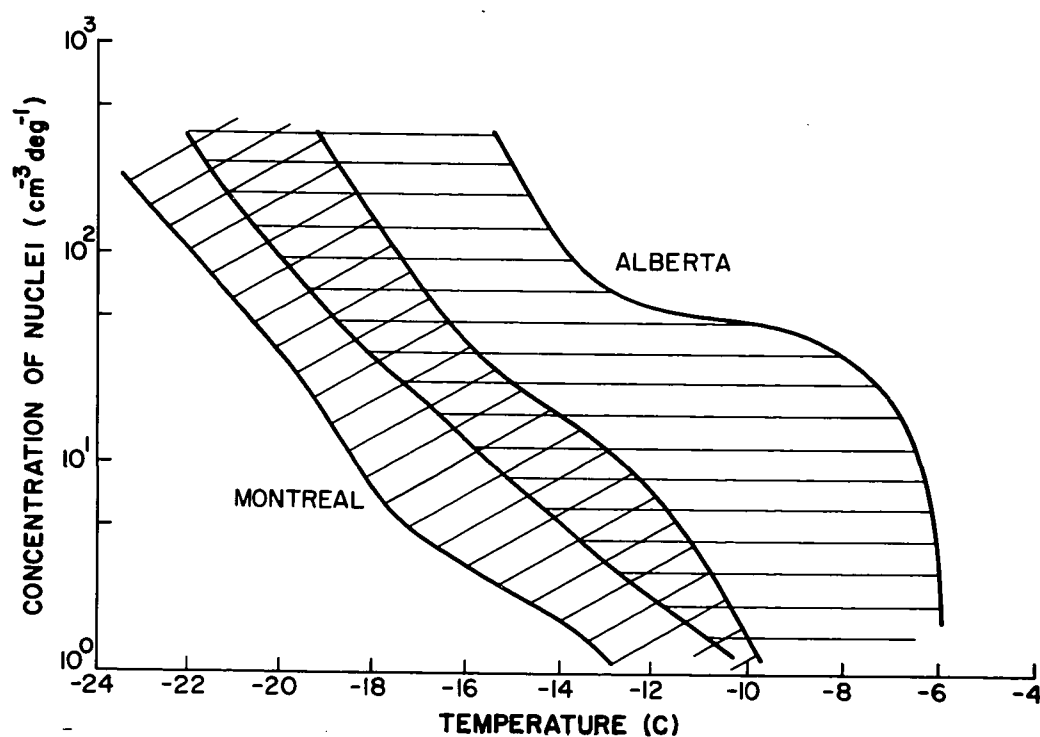
Figure 5-11.   Ranges of nucleus concentrations for summer rain from the Montreal area and from Alberta.

It may be concluded from the foregoing that the new measurements confirm the conclusions reached previously, namely, that the nucleus content is higher in hail than in rain, and that for both hail and rain, higher concentrations are found in samples from Alberta than in samples from Quebec and Ontario. The rapid change in nucleus concentrations between -4 C and -6 C appears to be characteristic of hail from Alberta. This feature also appears to a smaller extent in some of the rain samples from Alberta, but it has not been found in any of the other samples tested. Large changes in concentrations within narrow temperature intervals have been found in four cases at temperatures other than the range noted above. Three of these occur between -9 C and -10 C: a tenfold increase for a hail sample from Alberta, and
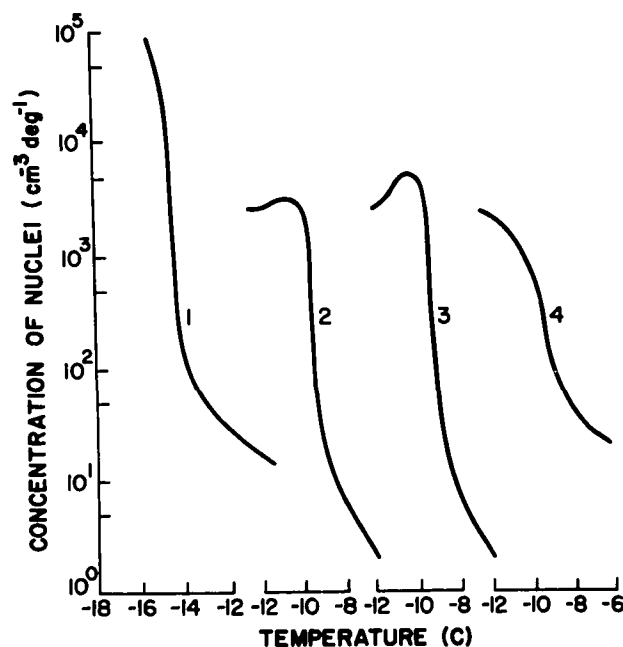
Figure 5-12. Nucleus spectra exhibiting abrupt changes; 1 and 4: hail from Alberta; 2 and 3: hail from Colorado.

abrupt changes from 10 cm^{-3} deg^{-1} to 4 x 10^3 cm^{-3} deg^{-1} in identical manner for two hail samples from Colorado. A very rapid increase of nucleus concentrations was found in one hail sample from Alberta: from 100 cm^{-3} deg^{-1} at -14 C to over 10^5 cm^{-3} deg^{-1} at -16 C. The nucleus spectra for these samples are shown in Fig. 5-12. Since the nucleus spectra for most samples were determined for the range 10^0 to 10^3 cm^{-3} deg^{-1} only, features such as those shown in Fig. 5-12 occurring beyond this range would not have been detected; such increases may be more common than indicated by the available data.

Peaks in the nucleus spectra of suspensions of surface soils near -5 C and the high concentrations of nuclei in hail at similar temperatures strongly suggest that the nuclei in the hail are generally of soil origin. The presence of other peaks in soil suspension has not been observed in the small number of soil samples that have been tested (cf. Chapter IV).

VI. RELATION BETWEEN MEASURED ICE NUCLEUS CONCENTRATION AND THE NUCLEUS CONTENT OF CLOUD WATER

The preceding two chapters have summarized the observational results on the concentrations of freezing nuclei in precipitation collected at the ground. It has also been shown that large fractions of these nuclei are smaller than 0.01μ in size. We now turn to the problem of how these observations can be related to the atmospheric processes that led to the results obtained, and what inferences can be drawn about the formation of the ice phase in clouds. Specifically, the contribution of freezing nuclei to the formation of ice will be examined; other processes, involving sublimation nuclei, fragmentation, acoustic and electrical effects, are not considered. Neither is an attempt made to follow the development of ice particles beyond their initial appearance.

A model to describe the entry of freezing nuclei into the precipitation will be developed and then used to estimate the freezing temperatures of cloud droplets and of raindrops. Attention is concentrated on convective summer storms typified by hailstorms in Alberta. The model is essentially this: Freezing nuclei are lifted from the surface into the cloud where diffusion to cloud droplets provides an efficient mechanism for the capture of these nuclei. The concentrations of freezing nuclei in cloud droplets and in raindrops are taken to be the same as the concentrations measured in the precipitation at the ground, and the freezing temperatures of raindrops and the concentrations of frozen cloud droplets are estimated on this basis.

The first step towards setting up the model outlined above is to examine the origin of the freezing nuclei that are found in the precipitation. This is a matter that requires consideration of the distribution of freezing nuclei in the atmosphere, and an examination of the processes of scavenging by the precipitation. To start with, it is assumed that freezing nuclei have a common origin with the majority of the atmospheric aerosols, at the surface, and that in general they follow the behaviour of other particulates. (The arguments that can be offered in support of this assumption are quite meagre at present; one can point to the similarity between the nucleus spectra of some precipitation samples and the spectra of nuclei for certain soil samples, to the reasonableness of the derived estimates of glaciation in light of available observations, and to the lack of well-founded alternatives. Further discussions on these points are presented in Chapter VII.) On this basis, the problem of the distribution and collection of freezing nuclei is made part of the more general problem of aerosol distribution and scavenging. These questions are therefore examined in some detail, with special emphasis on particles smaller than 0.01μ in diameter (see Sections 1 and 2 below). It is found that the concentrations of small particles are, from latest measurements, higher than was previously thought, and that reasonable account can be given of the particulate content of precipitation in terms of the aerosol content of the air in which the precipitation developed. The process mainly responsible for the collection of particles smaller than 0.01μ diameter and therefore of the majority of freezing nuclei is diffusion of the particles to cloud droplets.

With in-cloud capture of the freezing nuclei predominating,
the possibility is raised that the freezing nucleus concentrations
measured in the collected precipitation samples may be used to assess
the freezing nucleus content of cloud water, and therefore to estimate
the freezing temperatures of cloud droplets and of raindrops. In
Section 3 different aspects of the processes of precipitation develop-
ment are examined, to determine the extent of the agreement that can
be expected between laboratory results and events in the clouds.

1. ATMOSPHERIC CONCENTRATIONS OF 0.01μ DIAMETER PARTICLES.

The most useful information, from our point of view, comes from
measurements of Aitken nuclei, as the technique of measurement is
relatively simple, and thus a considerable body of data has been accumu-
lated. At the high supersaturations used in these measurements, particles
$10^{-3}\mu$ and larger can serve as centers of droplet growth; the measured
concentrations can therefore be taken to give a total particle count
(only small ions being excepted).

Typical results obtained by Hogan (1966), using continuous recording
instruments, are shown in Fig. 6-1. This graph indicates the variability
of the concentrations of Aitken nuclei both in space and in time. The
measurements for Fig. 6-1 were all obtained at the surface, and the
relation of the results to the type of environment and to seasons is well
represented here.
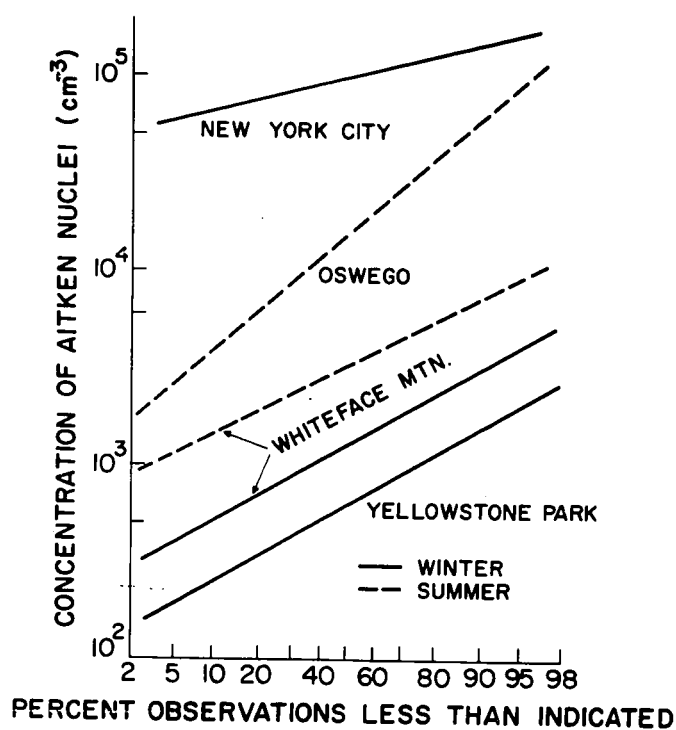
Figure 6-1. Cumulative frequency distributions of
Aitken nucleus concentrations at different locations.
Observation frequencies varied from a few minutes to
hours. (After Hogan (1966)).

Aitken nucleus concentrations in the free air under average

conditions were measured by Wigand (1919) and by Weickmann (1957) up

to altitudes of 6 km, and Junge (1961) reported on measurements from

6 to 27 km altitude. An average profile of the concentrations,

reconstructed from these sources, is shown in Fig. 6-2. There are two

layers of rapidly decreasing concentration; just above the surface and

above the tropopause. The first of these is a clear indication that

the surface is the major source of the Aitken nuclei, the second

indicates a discontinuity in the mechanisms of upward transport of

nuclei. Between 5 and 10 km and again over 20 km the concentration is

fairly constant. Junge (1961) explains the main features of the tropo-
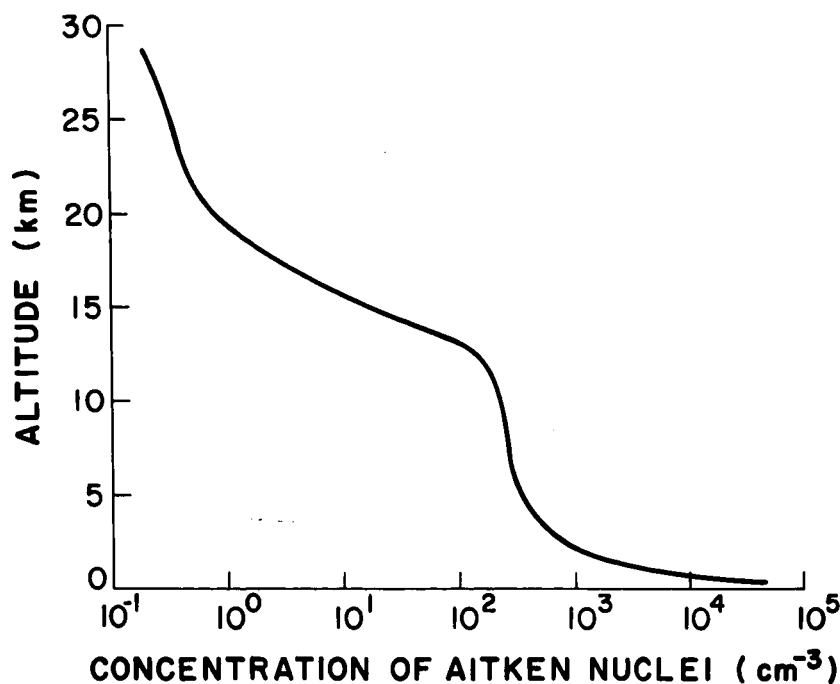
Figure 6-2. Smoothed profile of Aitken nucleus
concentrations between the surface and 27 km
altitude.

spheric part of the profile qualitatively on the basis of upward trans-

port through mixing and convection, with coagulation and capture by

precipitation as the removal processes.

The variation of average Aitken-nucleus concentrations with location

is from $< 10^2$ cm^{-3} in Alaska (Kumai, 1965) to $> 10^5$ cm^{-3} in populated

areas. Variations of up to two orders of magnitude are observed at any

given place with changing weather conditions. There is also a pronounced

diurnal variation observable at all locations, as shown by Hogan (1966)

and Clark and Whitby (1967) for populated areas, and by Went, Slemmons

and Mozingo (1967) for remote areas. This latter paper also demonstrates

that Aitken nuclei, at places away from anthropogenic sources, are produced

by photochemical processes from volatile plant products (mainly terpenes). Variability is also evident at higher altitudes in the free air (Fenn, Gerber and Weickmann, 1965; Weickmann 1957, 1966).

As mentioned earlier, Aitken nucleus measurements can be taken to represent the total concentrations of particles. The lower threshold for the sizes of particles involved is difficult to ascertain, and is in fact variable, depending on the composition of the aerosol and on the experimental technique. Hosler (1950) set this limit at $5 \times 10^{-3} \mu$ from electronmicroscope examination of the droplet residues. Since the concentration of particles decreases rapidly above $10^{-2} \mu$ diameter (see next paragraph), the Aitken nucleus count is nearly equivalent to the concentration of particles from $5 \times 10^{-3} \mu$ to $10^{-2} \mu$ diameter.

Information on the size distributions of aerosols smaller than $10^{-2} \mu$ has only recently become available. Clark and Whitby (1967) reported on the measurements of particle concentrations in an urban environment over the size range $10^{-3} \mu$ to 3μ. These were obtained by the simultaneous use of three different types of instruments, each covering a different part of the size spectrum. Figure 6-3 shows one such spectrum. Particle concentrations increase with decreasing particle size even for particles smaller than $10^{-2} \mu$, in notable contrast with the results of several previous investigators (Junge, 1963; Pasceri and Friedlander, 1965). Inefficiency of the older methods for the detection of small particles was suggested as the explanation for this disparity.

CONCENTRATION PER DIAMETER INTERNAL

10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0

10^{-3} 10^{-2} 10^{-1} 10^0

PARTICLE DIAMETER (μ)
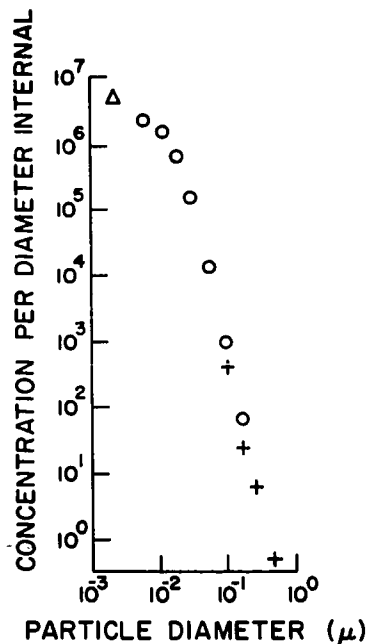
Figure 6-3.   Particle size distribution after Clark
and Whitby (1967). The different symbols for the
points denote the types of instruments providing
the readings: $\triangle$ - condensation nucleus counter,
O - electrical counter, + - optical counter.

The distribution in Fig. 6-2 describes the long-term equilibrium

concentrations that are established through numerous processes. For

consideration of the cloud-aerosol interaction in a developing cloud,

it is necessary to take into account the short-term evolution of the

aerosol as the air carrying it rises from the surface up to cloud

levels, where the environmental concentration of particles may be 100

times lower than at the surface. There are three factors that affect

the concentration and the size distribution of the aerosol in ascending

air before formation of cloud: expansion, mixing and coagulation.

Expansion reduces the total concentration by a factor of less than two

for the average height of summer storms. Mixing will tend to reduce the total concentration of the aerosol, but the importance of mixing can be expected to diminish with increasing size of the storm. Expansion and mixing affect equally particles of all sizes.

The theoretical treatment of the changes in size distribution that occur in a closed system due to coagulation was given by Junge (1957); the results of his computations are shown in Fig. 6-4. As shown by this graph, the concentrations of very small particles diminish rapidly with time; however, for particles greater than $5 \times 10^{-3} \mu$ diameter, the reduction in one hour would not be more than a factor of two. The reductions in the concentrations of small particles in air lifted from the surface would, in fact, be even smaller than indicated by this figure
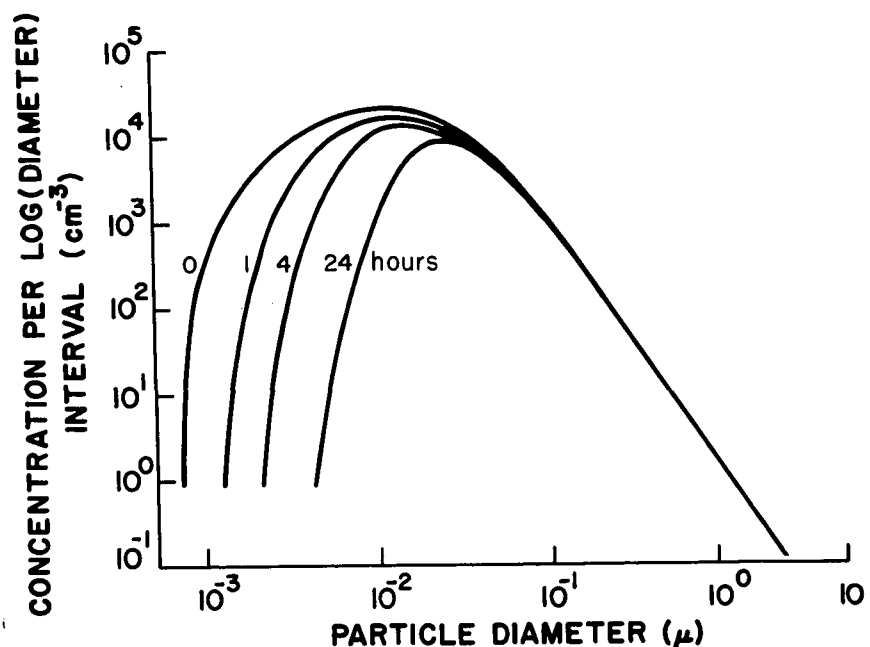
Figure 6-4. Change of size distribution with time. Initial distribution (t = 0) was taken from measurements. After Junge (1957).

for three reasons: (i) If there is a reduction of the total particulate content of the air due to mixing, the rate of coagulation is reduced. (ii) There is some production of small particles even above the surface; condensation of gaseous constituents provides one such source (Went et al., 1967). (iii) The initial concentrations of small particles are higher, according to Fig. 6-3, than what was assumed in Fig. 6-4, and the rate of coagulation decreases with increasing negative slope of the spectrum. Distributions of the type presented in Fig. 6-3 were shown by Clark and Whitby (loc. cit.) to be "self-preserving" or time-independent. It thus appears unlikely that the size distribution of an aerosol would be greatly modified in the 10-30 min time interval that air takes to rise from the surface to cloud heights.

Measurements of the concentrations of Aitken nuclei in the atmosphere provide evidence that high aerosol concentrations are associated with convective activity. Selezneva (1965) reported that the concentrations of Aitken nuclei, on days with cumulus clouds, decreased with height (to 6 km altitude) in an exponential form with a decay-constant of 1 km. This is about 3 times greater than the average decay-constant in Fig. 6-2, for heights up to 2 km. At a typical cloud base height of 1.2 km (in Alberta) the concentration of particles would thus be about 30% of the concentration at the surface. These measurements were obtained in cloud-free spaces; the concentrations are likely to be even higher directly in an updraft, before the formation of cloud.

Weickmann (1966) reported that inside small cumuli the concentrations of Aitken nuclei were about 4 times higher than in the surrounding air. Admirat and Soulage (1966) found ice nucleus concentrations 10 times

higher than ambient concentrations at the bases of clouds. Auer (1967)
measured the concentrations of condensation nuclei just below the bases
of fair weather cumuli and found that the concentrations of nuclei
active at supersaturations of 1% were as high as 10^3 cm^{-3} on occasion.
According to Jiusto (1967), particles active at 1% supersaturation are
about 0.1 μ in diameter, so that the concentrations of 0.01 μ diameter
particles would be about 10^6 cm^{-3}.

In light of the foregoing, the total concentration of particles in
a convective parcel of air may be expected to be of the same order of
magnitude as concentrations measured at the ground: 10^4 to 10^6 particles
per cm^3 can be realized, particularly with strong winds and with dry and
loose soil at the surface.

2. SCAVENGING OF AEROSOLS BY CLOUD DROPLETS AND PRECIPITATION

In this section the roles which different processes play in pro-
ducing the concentrations of freezing nuclei found in the precipitation
are examined in order (i) to estimate the extent to which the observed
final concentrations reflect the concentrations of nuclei in the cloud
and raindrops aloft and (ii) to estimate the rate at which particles
are collected by the cloud droplets in a developing cloud.

It has been shown by Greenfield (1957), Hess (1959) and Junge (1963)
that the most important processes for the removal of particulates from
the air in precipitating clouds are: the capture of particles smaller
than 0.1 μ diameter due to diffusion to cloud droplets, and the collec-
tion of particles larger than 1 μ diameter by falling raindrops and ice
particles. The contributions of these processes to the freezing nucleus
content of precipitation are discussed in parts (a) and (b) of this section.

a) Concentrations of freezing nuclei in the precipitation at the
    ground and in the clouds.

Since it is proposed to estimate the glaciating behaviour of clouds

from the concentrations of freezing nuclei in precipitation collected at

the surface, it is important to establish the extent to which such con-

centrations are affected by the nuclei collected in the sub-cloud layer

by the falling precipitation.

The collection efficiencies of falling raindrops are negligible

for particles below about 1 μ diameter, due to the streamline flow of

the small particles around the drops. Calculations by Langmuir (1948)

and by Pearcey and Hill (1957) show that the collection efficiency of

millimeter-sized drops exceeds 10% only for particles which are larger

than 4 μ diameter, and reaches 80% for particles approximately 10 μ

in diameter. Experimental work by Goldsmith et al. (1963) on the radio-

activity of precipitation (originating mostly from 0.1 μ to 1 μ particles)

and by Georgii (1965) on the ion content of rain suggest that collection

efficiencies are in fact higher than calculations indicate, but no

quantitative results are available. The overall effect of washout depends

also on the type of precipitation (dropsize distribution, rain intensity

and duration) and on the rate of re-generation of the aerosol in the sub-

cloud layer.

In view of these complications, it might be useful to first assess

what the maximum effect could be. To this end, let us assume 100%

collection efficiency for particles greater than 1 μ diameter and take

the concentrations of particles of these sizes to be 1 cm^{-3} everywhere

below the cloud (see Fig. 6-3). One cm^3 of collected rainwater, if it

originated in 1 mm raindrops which fell from the cloud base at 1.5 km, and assuming no overlap of the spaces swept by the drops, would then contain about 10^6 particles. Recalling from Chapter IV that the probability for a 0.01μ diameter particle to be an active nucleus at temperatures above -10 C is about 10^{-11}, and again assuming this probability to vary in proportion with the surface area of the particle, it is estimated that 1 out of 10^7 particles of 1μ size would be active freezing nuclei. Thus, the maximum possible concentration of freezing nuclei (at -10 C) in rain which could result from sub-cloud washout is of the order of 0.1 cm^{-3}. Measured concentrations of nuclei at -10 C in rain are from 0.1 cm^{-3} to 10 cm^{-3}, indicating that washout is possibly, but not likely, a significant factor in influencing the nucleus concentrations at the ground.

The fact that only large particles are expected to be collected by the falling raindrops provides a convenient way to estimate what contribution to the freezing nucleus content is made by sub-cloud collection. Filtering the samples through filters of 1.2 μ pore size has been found to result in reductions of nucleus concentrations which did not exceed a factor of 2, with no noticeable variation in the degree of reduction at different parts of the nucleus spectra. Since some of the observed reduction on filtering is due to the removal of particles smaller than the pore size, the change in concentrations between filtered and non-filtered samples is an upper limit for the contribution of large particles to the nucleus content of precipitation samples.

A doubling of nucleus concentrations thus appears to be the maximum effect that can be expected due to sub-cloud collection of nuclei. For a typical nucleus spectrum, a factor 2 change in concentration corresponds to a 1 deg difference in temperature. It can therefore be concluded that the assumption that the nucleus content of cloud water is the same as the nucleus content of rain collected at the ground does not lead to errors greater than 1 deg in the freezing temperatures estimated for the cloud.

In an experiment designed to confirm the conclusion reached in the previous paragraphs, a sample of cloud water was collected by means of a collector attached to an aircraft. This sample was found to have higher concentrations of freezing nuclei than most precipitation samples. No simultaneous sample at ground level was available and the collection method used in the aircraft has not been tested previously; the experiment is therefore not conclusive, but the feasibility of this type of experiment has been demonstrated and further effort in this direction seems warranted.

The amount of particulate matter collected by hailstones during fall from cloud base to ground is negligible for two reasons: the collection efficiency of hailstones larger than 5 mm diameter for all micron-sized particles is minute and the large mass of the stones would tend to mask the effects of contamination on the surface when the stone's melt is analyzed. In any case, the outer layers of hailstones were removed before analysis, so that the measured concentrations of nuclei in hailstones are certainly good indicators of the nucleus content of the cloud water from which the stones developed.

b) Rates of capture of particles by diffusion.

Coalescence of the particles with cloud droplets due to Brownian diffusion is the major process for capture of particles below 0.01 μ in size.

Following Greenfield's (1957) modification of the diffusion equation derived by Whytlaw-Grey and Patterson (1932), the rate of change of the concentration of particles, n_p (cm^{-3}), in a cloud with droplet concentration n_c (cm^{-3}) is

$$- \frac{dn_p}{dt} = K_B n_p n_c$$

where K_B is the coagulation constant and is given by the expression

$$K_B = 7.8 \times 10^{-11} \frac{d_c}{d_p} \left(1 + \frac{1.92 \times 10^{-5}}{d_p} \right) \quad (cm^3 sec^{-1})$$

with d_p and d_c denoting the diameters of the particles and of the cloud droplets respectively (in cm). The form of K_B given above is valid for $d_p \ll d_c$. The numerical constants are given for a pressure of 525 mb and a temperature of -10 C (corresponding to typical conditions in Alberta at 4.25 km altitude). The physical interpretation of K_B is that it gives the volume of space from which particles of the size considered are removed by one cloud droplet in every second. For consideration of the rate at which particles are removed from the air, it is convenient to define the average life of the particles:

$$\lambda = \frac{1}{K_B n_c} \quad (sec)$$

Figure 6-5 shows the relation between average life, particle size and cloud parameters for selected ranges of the variables.
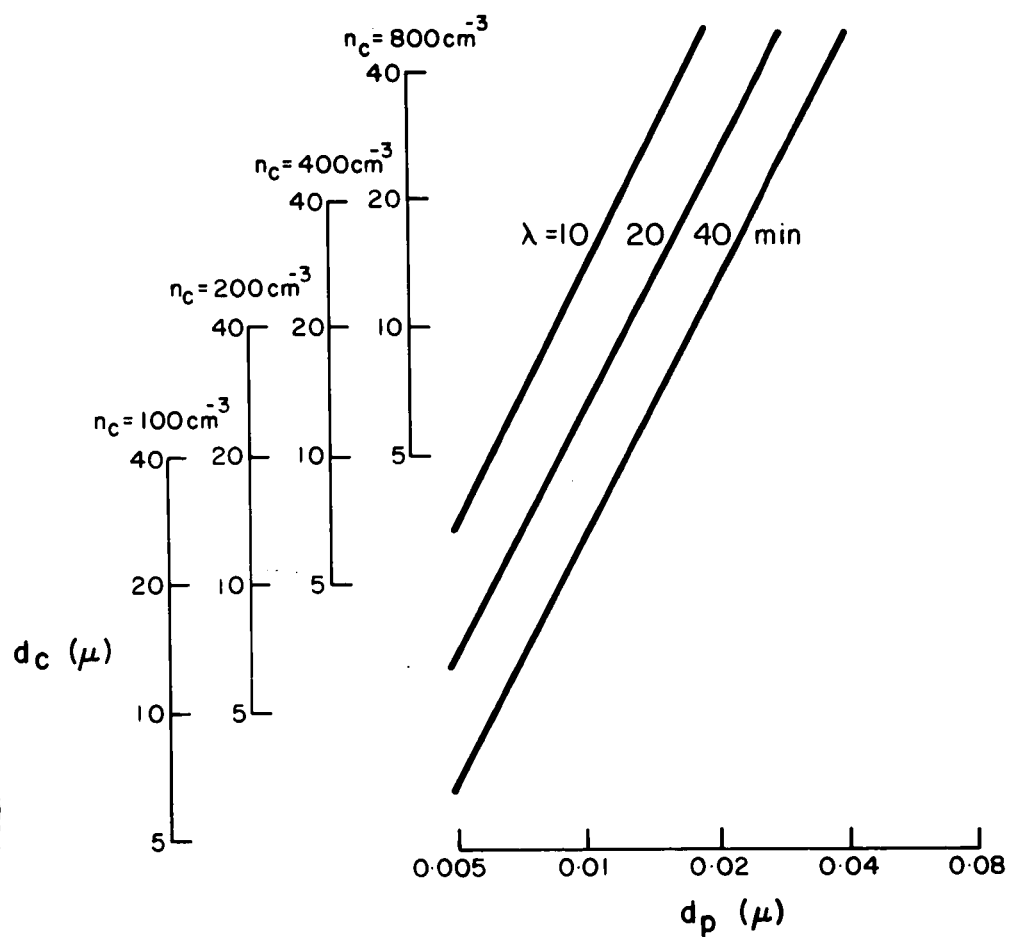
Figure 6-5.   The relation between size and average
life of particles in clouds of different composition.
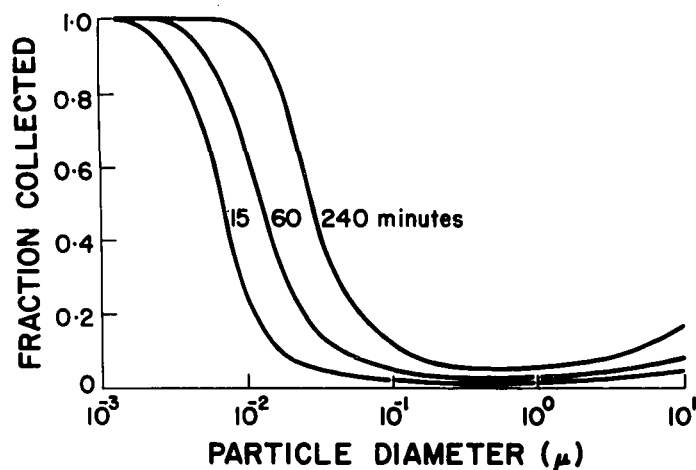
Figure 6-6.   Calculated rates of capture for particles
of different sizes.

The effect of particle size on the rate of capture is better illustrated in Fig. 6-6 which gives the fraction of particles collected in the times indicated by a cloud with n_c = 200 cm^{-3} and d_c = 10 μ. The collected fraction of particles of different sizes changes fairly abruptly with size, and the size at which this "cut-off" occurs increases with time. The formation of precipitation in convective storms takes place fairly rapidly, in 15-60 minutes; the importance of particle size for efficient removal by the cloud is therefore pronounced. This point is further dealt with in the next section.

To demonstrate that capture by diffusion can account for the concentrations of particles in the precipitation, the concentrations in the air and in the precipitation can be compared. The concentration of particles below 0.01 μ size in rain and hail is 10^{10} to 10^{12} cm^{-3} (cf. Chapter IV). In the updraft of a storm the concentration of particles is estimated to be 10^4 to 10^6 cm^{-3} (cf. Section 1 of this chapter). Taking the amount of precipitation that originates in 1 m^3 of air as 1 cm^3, and assuming 15 min for the time of mixing of the aerosol with the cloud (20% of particles collected according to Fig. 6-6), the concentration of particles in the precipitation resulting from capture by diffusion is found to be 2 x 10^9 cm^{-3} to 2 x 10^{11} cm^{-3}, in agreement with the observed range of concentrations.

From the foregoing considerations, it may be concluded that diffusion to cloud droplets is the major source of small particles for the precipitation. Because of the large numbers of small particles relative to larger ones, the majority of freezing nuclei are small, even though the

chance for a particle to be a freezing nucleus decreases with size

(cf. Chapter IV). Thus, diffusion to cloud droplets provides the

main mechanism for the entry of freezing nuclei into the precipitation.

Other processes are of minor importance only. Sub-cloud accretion by

falling raindrops and hailstones has already been discussed. In addition,

large ($>$ 0.01 μ) particles may enter the precipitation by coalescence

with cloud droplets due to turbulent diffusion or by serving as conden-

sation nuclei. The first of these processes has been shown by Greenfield

(1957) to give rise to the scavenging of less than 10% of the available

particles in the air under typical conditions. Condensation nuclei are

mostly soluble, although Jiusto (1967) found that many other types of

particles can act as condensation nuclei, contrary to expectations based

on the macroscopic properties of these substances. Some particles may

therefore be expected to serve both as condensation nuclei and freezing

nuclei. In any event, the contribution that these processes make to

the freezing nucleus content of precipitation can be separated from the

freezing nuclei caught by diffusion on the basis of particle sizes.

The nucleus spectra obtained with filtered samples represent the freez-

ing nucleus content of cloud water, and the differences between the

concentrations of nuclei in unfiltered and filtered samples are the

contributions of sub-cloud collection and other processes. The important

point established in the preceding sections is that the observed high

proportions of small nuclei can be explained on the basis of the relative

efficiencies of the different scavenging processes.

3. FREEZING NUCLEUS CONTENT OF DEVELOPING PRECIPITATION.

In the previous sections we have examined the ways in which freezing nuclei are most likely to enter the precipitation. It was found that diffusion of particles of less than 0.01μ diameter to cloud droplets is the most important of the collection processes. The predominance of this process raises the possibility that the results of the laboratory determinations of the freezing nucleus content of precipitation may be used to estimate the freezing temperatures of cloud elements. It will now be examined whether a one-to-one correspondence between the number of freezing nuclei that are found to be active above some temperature in a sample of precipitation and the number of nuclei that initiate freezing in a cloud at the same temperature can reasonably be expected to exist or not. In other words, those influences which the processes of precipitation development themselves have on the formation of ice particles will be considered, given that the process for the capture of ice nuclei is diffusion to cloud droplets.

If a long time were available between the formation of a cloud and the onset of the further processes of precipitation formation, so that complete scavenging could take place, and if the precipitation mechanisms were simple rearrangements of drop sizes with the freezing of some of the drops as the temperature is lowered, a description of the freezing characteristics of this cloud could be readily given. Real situations, in which the details of the precipitation processes cannot be neglected, present a number of complications:

(a) The rates of capture of nuclei are not negligible with respect to the development times of precipitation.

(b) The liquid water content of clouds is not constant throughout the formation of precipitation.

(c) The growth of precipitation elements may lead to the preferential collection of frozen or non-frozen hydro-meteors.

(d) Freezing nuclei may be subject to influences that result in different performances in the laboratory experiments and in the cloud.

The approximate magnitudes of these effects are considered in the following sections.

a) <u>Effect of scavenging rate on freezing nucleus content</u>.

The rate of capture of particles by diffusion to the cloud droplets has been calculated in Section 2b of this chapter (cf. Fig. 6-5). A typical value for the average life of 0.01 μ diameter particles, in a cloud with 400 droplets per cm^3 and of 10 μ diameter, is 20 minutes. Under these conditions, it would take 46 minutes to have 90% of the nuclei available in the air caught by cloud droplets. For smaller particles and for denser clouds this time would be reduced.

The growth of precipitation, from the time cloud forms at the condensation level to the time the precipitation falls out of the cloud, takes approximately 15 min to 1 hour in convective storms, and probably longer in continuous types of precipitation. During its growth, a raindrop, for example, collects cloud droplets which have had differing times available for the collection of ice nuclei; thus part of the raindrops' volume originates from cloud drops that have collected relatively few particles (freezing nuclei) and part from cloud droplets

that were in regions of cloud where practically complete scavenging has taken place.

Taking 30 minutes as the average time of mixing of cloud and aerosol, the reduction of the nucleus content of the precipitation, compared to what an estimation of nucleus content based on total scavenging of nuclei in the air would yield, amounts to 22%. This is a minor factor, and it seems reasonable to neglect it.

In order to estimate freezing behaviour in the clouds from the nucleus concentrations measured in the precipitation, the nucleus content of the precipitation at the end of its development should be compared with the nucleus content of the cloud water at intermediate stages of precipitation development. Taking five minutes as the time required for a cloud to be lifted from the condensation level to a height where the temperature is -5 C, the concentration of nuclei in the cloud water when this level is reached is only 20% of the concentration that the precipitation acquires after total scavenging of nuclei has taken place.

b) Dilution due to continued condensation.

Precipitation elements continually grow by condensation as they are lifted in an updraft. This constitutes a dilution of the concentrations of captured particles compared to the concentrations that would be reached for a droplet of unchanged volume.

Typical values of the liquid water contents in the cores of convective storms in Alberta are 1 g m^{-3} at the freezing level (3 km above surface) and a maximum of 3 g m^{-3} occurring at approximately 7 km altitude. Combining this increase with the fact that due to the expansion of the air there are fewer drops in each m^3 of air at the higher altitude, the volume increase of drops resulting from condensation is found to be approximately five-fold.

The increase in the sizes of the cloud droplets enhances their rate of collection of particles, but since this rate is proportional to the diameter of the droplet and does not balance the volume increase, the concentration of particles in a drop will be lower after growth than it would be without the additional condensation.

The further development of the precipitation will not greatly modify the concentration of particles. Some condensation may be taking place even after the droplets are removed from the updraft, due to the temperature lag of falling drops, but is likely to be a relatively minor factor.

It is seen from the foregoing that the continued scavenging of nuclei in the cloud leads to higher nucleus concentrations in the precipitation than those existing in the cloud water just after formation, and that dilution has the opposite effect. The magnitudes of the effects depend on cloud conditions; however it may be assumed that the net effect of the two processes is small.

c) Preferential collection of frozen or non-frozen cloud droplets.

If, during the development of precipitation, only liquid or only solid hydrometeors could contribute to the growth of a precipitation element, a bias would be introduced into the spectrum of freezing nuclei in the precipitation by excluding or amplifying the relative proportions of nuclei that were active at temperatures warmer than the temperature in the region of cloud in which this type of growth occurred.

The development of frozen hydrometeors could lead to preferential collection through the collection of supercooled droplets and the rejection of frozen ones. Hailstones developing from a cloud droplet

that froze at a fairly warm temperature are important examples for
this effect. Calculations of hail growth by English (1966, private
communication) indicate that hailstones reach 30-60% of their final
volume while the growth is dry (i.e. all of the hailstone is frozen
and it is usually assumed that during dry growth only liquid droplets
can be accreted. The higher figure of 60% applies to growth in high
concentrations of accumulated rainwater. The lower figure, 30%, applies
if the growth environment consists of cloud droplets. The temperatures
at the transition points, where the falling hailstones enter the wet
growth regime, are -8 to -15 C for growth in high liquid water content
environments and -15 to -20 C for growth without high rain concentrations.
From these figures it appears that in the most extreme case, the inner
60% of a hailstone's volume may be devoid of freezing nuclei active
above -15 C, except for the one nucleus which initiated the hail form-
ation. However, no such effect was evident from the examination of the
freezing nucleus contents of different layers of hailstones, indicating
that either the growth conditions that gave the extreme values quoted
are unrealistic, or that frozen droplets are also accreted by hailstones.

A raindrop growing by coalescence will remain liquid until it reaches
the temperature of activity of one of the freezing nuclei in the drop
or until it collides with a frozen cloud droplet. During growth in the
liquid state, no preferential collection occurs. Rain, in general, might
originate from graupel, small hail or snow, as well as from liquid drops,
and it seems rather difficult to assess the possible importance of biased
collection in these rain-forming processes.

Aggregation of snowflakes may constitute a preferential collection of frozen particles (crystals) which would lead to an undue increase in the concentrations of nuclei active at temperatures warmer than the temperature of the growth region.

For hail and for rain (other than that originating as snow) the overall effect of preferential collection is clearly to lead to lower concentrations of nuclei in the precipitation than in the cloud water. The concentrations of freezing nuclei in hail are usually higher than in rain or snow. The effect here discussed would tend to cause differences in the opposite direction. To resolve this contradiction, attempts should be made to relate the nucleus content of hailstones with structural evidence for dry growth.

d)   Changes in activity of freezing nuclei.

Freezing nucleus concentrations determined from the laboratory experiments have been assumed to be representative of the performance of nuclei in the natural environment. There seems to be little cause for doubting the validity of this assumption, but some secondary effects may be pointed out.

It has been confirmed repeatedly that the measurements reflect the properties of the samples investigated and are not influenced by the experimental arrangements (cf. Chapter II). There is no evidence to indicate that drops in free fall would behave differently from stationary drops with respect to freezing initiated by nuclei suspended in the drops. Electrical fields in the clouds may have an effect on freezing nuclei, but this has not been investigated so far.

Aging of freezing nuclei, reduction in activity with time, has been observed for water samples stored at temperatures above 10 C, but the reduction in concentrations usually amounted to only about a factor of 2 after periods of weeks. This rate of aging is quite negligible. However, the rate of aging for a nucleus within the first few minutes, or perhaps seconds, after its immersion is still unknown.

The development of nucleation activity of immersed particles by etching of the surfaces of particles, or by breakup and consequent exposition of new surfaces may also occur.

It has been suggested by Bigg (1965) that freezing nuclei may get coated in the atmosphere with hygroscopic material, which produces a brine when humidity is increased, and the nucleus therefore becomes active only when the drop grows sufficiently large to reduce the concentration of the dissolved material. However, in our model the most likely way for freezing nuclei to produce ice particles is the capture of the nuclei by cloud droplets; the effect of contaminants in this case would be minimal.

To summarize the findings of this chapter, the following points may be emphasized:

1) In an updraft, the concentration and size distribution of the particulate content of the air will not be greatly modified in the time the air moves from the surface to cloud heights.

2) The observed average proportions of small ($< 0.01 \mu$ diameter) and large freezing nuclei in precipitation are in agreement

with the concentrations estimated on the basis of capture of
small particles by diffusion to cloud droplets and the collec-
tion of larger particles by falling precipitation.

3) The influence of the process of precipitation development on
the nucleus content may be neglected as a first approximation,
and the nucleus content of cloud water and of raindrops may be
taken to be the same as the nucleus content measured in the
precipitation collected at the ground.

VII.   DISTRIBUTION OF ATMOSPHERIC ICE NUCLEI

Before proceeding to use the model which was developed in the previous chapter to describe the entry of freezing nuclei into the precipitation, it seems important to reconcile this model with the observations on atmospheric ice nuclei. We have assumed that freezing nuclei form part of the general particulate matter in the atmosphere with respect to distribution and collection by precipitation. On the other hand, the presently available literature on atmospheric ice nuclei suggests that the general pattern of behaviour of particulates is not followed by ice nuclei. Possible ways to resolve this conflict are examined in this chapter.

Mossop (1963) and Dufour (1966) have given exhaustive surveys of the large variety of observations concerned with atmospheric ice nuclei. The main conclusion on the spatial distribution of ice nuclei is that a fair degree of world-wide uniformity of concentrations seems to exist. Bigg (1965) found no appreciable differences in the concentrations measured at widely different points around the globe. Kline (1963) detected maximum differences of one order of magnitude in the average concentrations of nuclei at ten stations across continental U.S.A. Mossop (1963) reported that no systematic decrease of ice nucleus concentrations with altitude could be deduced from measurements in the free air. Experiments on mountain peaks (Georgii, 1959, Price and Pales, 1964) have not given significantly different results from low altitude measurements. Simultaneous increases of concentrations (approximately three-fold) over distances of several hundred kilometers have been reported by Droessler (1965) and Soulage (1966).

Fluctuations of ice nucleus concentrations measured at fixed locations have been reported by numerous investigators. In measurements taken few minutes apart, the concentrations of nuclei usually vary within a factor of less than ten. Occasionally, increases of greater magnitude (up to factors of 100) and lasting for periods of 1-10 hours have also been noted (see summary by Bigg, 1961). Smaller increments, factors 2 to 5, have been shown to coincide with dust storms in a number of cases (Schaefer, 1954; Isono et al., 1959; Gagin, 1965). Diurnal and annual cycles of variations have also been reported, but not firmly established.

The overall picture that thus emerges from the literature on atmospheric ice nuclei is not a very clear one. It is evident, however, that on the one hand the measurements indicate much greater constancy for the concentrations of ice nuclei than exists for most other meteorological variables, and on the other hand, fluctuations exist which are more rapid and more intensive than the variations of other known parameters. This is not the case for the total particulate content of the atmosphere, as the main features of the variations in concentrations of Aitken nuclei (which well represent the concentrations of all particles) are fairly well understood in terms of their origin and transport mechanisms. It is therefore often stated that ice nuclei do not follow the patterns of the distribution of particulates. Simultaneous measurements of the concentrations of ice nuclei and of particles have been mostly inconclusive; weak correlations with one or another component of the aerosol content have been found in some experiments, but were lacking in others. The explanation frequently suggested for this lack of

correlation is that ice nuclei enter the troposphere from strato-

spheric storage regions (possibly from extraterrestrial sources) in

contrast to the surface origin of particulates (Bigg, 1965;

Droessler, 1965). It has also been suggested that interactions

between ice nuclei and other components of the atmospheric aerosols

may occur in such a way that a net balance is established for the con-

centrations of effective ice nuclei. However, another aspect of the

problem is brought out by our results: arguments will be given below

to show that from the freezing nucleus content of precipitation samples,

correlation between particulates and freezing nuclei can be expected

to be strongest for nuclei active at temperatures warmer than about

-15 C, and the techniques of ice nucleus measurements used in the past

were inadequate for the efficient detection of such nuclei. It is there-

fore suggested that there should be a close relation between ice nuclei

and particulates of surface origin, and that this relation has not been

observed in the past mainly because of deficiencies in the observational

techniques. Extraterrestrial or stratospheric sources and ice nucleus-

aerosol interactions may be important in establishing the concentrations

of ice nuclei active at temperatures below -15 C, although it would seem

likely that the process responsible for the generation of more active

nuclei (particulates of less than $0.01\,\mu$ size and of soil origin) would

also exert an influence at the lower temperature regions. The details

of these arguments are presented in the following paragraphs.

A re-examination of the results of atmospheric ice nucleus measurements is warranted on the basis that there are major differences between our approach to the problem and those previously used. Three points can be mentioned in this regard:

(i) Measurements of the concentrations of ice nuclei in the air reflect the environmental conditions in which the precipitation develops. Our measurements on the freezing nucleus content of precipitation provide information on the final product of the precipitation process. Determining the properties of the precipitation, rather than of the ambient air in which the precipitation developed, has the advantage that the precipitation contains information directly from the region of its origin; this could be matched only by measurements of airborne concentrations directly in the air in which a cloud is about to be formed.

(ii) The majority of previous results originated from cloud chamber experiments, and some from the so-called millipore filter technique (Mossop et al., 1966). The action of ice nuclei in these techniques is greatly influenced by such factors as supersaturation, concentration of hygroscopic particles, the density and persistence of the cloud, and other minor factors. Due to these, it is difficult to determine whether the ice crystals that develop have been initiated by freezing nuclei (from the liquid phase) or by sublimation nuclei (from the vapour phase). It is equally difficult to estimate how natural processes would compare with the experiments with respect to the factors mentioned. In our drop freezing experiments there is no ambiguity to the mode

of ice formation - nucleation is by particles suspended in the

bulk water. Furthermore, the efficiency of detection of nuclei

is not dependent on temperature in these experiments and there-

fore reliable information can be obtained at any temperature

below 0 C. The sensitivity of cloud chamber and millipore

techniques is adequate only below about -12 C.

(iii)Our results indicate that particles smaller than 0.01μ contri-

bute large fractions of the freezing nucleus content of preci-

pitation samples. Previous measurements have been biased

towards larger sizes on the belief that ice nuclei are larger

than 0.1μ .

On the basis of these considerations, it is believed that measurements

of the freezing nucleus contents of precipitation samples reveal

aspects of the distribution and activity of atmospheric ice nuclei

that could not be obtained by other presently available methods.

From an examination of the measured nucleus spectra presented in

Chapter V, it is immediately evident that there is a wide range of

variation in concentrations for the different samples. The range of

concentrations at -10 C is from 1 cm^{-3} to 500 cm^{-3}. However, no

correlations between these variations and other relevant parameters has

been established so far. An attempt by Schlien (1967) to find geograph-

ical differences in nucleus content, by examining samples from a network

of collecting stations across Canada, has given negative results.

Bishop (1968) has found differences of one order of magnitude in concen-

tration between samples collected from the same storm 15 minutes apart.

It is noteworthy that the greatest differences in the nucleus content of precipitation samples are found at temperatures above -12 C. The high nucleus contents at warm temperatures are always associated with S-shaped nucleus spectra - a levelling off of the spectra at around -10 C followed by more rapid rise at temperatures below -15 C (cf. Chapter V). These spectra are quite similar to those obtained for soil samples containing efficient freezing nuclei.

From the large variations in nucleus content, especially at warm temperatures, it would appear that the ice nucleus content of the troposphere is by no means homogeneous. Some of the variations are undoubtedly caused by differences in the effectiveness of the scavenging processes in different clouds, but this effect is expected to be small for particles below 0.01μ in size due to the fast rate of removal of these particles by cloud droplets (cf. Chapter VI). It seems more likely that the variations in nucleus content are related to variations in the particulate content of the air in which the clouds formed. The tendency of hail samples to have higher concentrations of nuclei than rain, and of summer rain to have higher concentrations of nuclei than winter rain (Bishop, 1968), support this idea and point to the importance of convection in transporting nuclei originating at the surface to the clouds.

Some of the results from other investigations can be interpreted as evidence for the kind of variations that appear to be present in precipitation samples. Bigg and Meade (1959), Bourquard (1963), Price and Pales (1964) and Isaac (1968), among others, have detected fluctuations in concentrations of ice nuclei up to a factor of 100 over periods

of minutes. Isaac's results were obtained during thunderstorms.

Precipitation samples frequently contain numerous freezing nuclei active at temperatures between -5 C and -10 C. It is estimated (cf. Chapter IX) from these measurements that the concentration of nuclei in the air in which the precipitation formed may have been as high as 10^3 m^{-3} for nuclei active above -10 C and 10^2 m^{-3} for activity at -6 C. Cloud chamber measurements usually do not detect measurable activities at these temperatures, and the above concentrations are reached only at temperatures of -15 C or colder. The reasons for this disparity would appear to be that high concentrations such as those detected in the hail samples probably occur only in very limited regions, such as intense updrafts, and in the inefficiency of the cloud chamber (and millipore) methods at warm temperatures. The main cause of this inefficiency is that the time of mixing of the aerosol with the cloud in the instruments is short compared to what would be required for the small freezing nuclei to be captured by the cloud droplets. Warner and Newnham (1958) have measured the rate at which the number of ice crystals increased in a chamber in which the cloud was continually maintained and found this to increase roughly exponentially with a time constant of 6 minutes. The time constant for the collection of $0.01\,\mu$ diameter particles is given by Fig. 6-6 for the reported cloud conditions as 10 minutes; the closeness of the two rates would indicate that the time lag in nucleation may have been almost entirely due to the gradual capture of the nuclei. Most cloud chambers use approximately 2-minute observation times with the clouds persisting for even shorter times in some cases.

The clouds usually employed are also less dense than that used by Warner

and Newnham, especially at warm temperatures. It thus seems inevitable

that most cloud chamber measurements yield results that are underesti-

mates, with the efficiency decreasing towards warmer temperatures.[*]

This conclusion is supported by the observations of Georgii (1959) and

Rau (1955) who, by using long measuring times with their cloud chambers

and continually maintaining the cloud within them, obtained temperature

spectra very similar to the S-shaped spectra of freezing nuclei in hail

samples. Tentative evidence of the inefficiency of a cloud chamber for

the detection of freezing nuclei was also presented by Vali (1967) from

a comparison of cloud chamber measurements on an aerosol with those

obtained by transferring the aerosol to bulk liquid for drop freezing

experiments.

Emphasis has been put in this chapter on the variability of freez-

ing nucleus concentrations and on the possibility that this is related

to the surface origin of the nuclei. One should add to this the finding

that some surface soils have been found (cf. Chapter IV) to be very

good sources of nuclei active above -8 C, with considerable fractions of

these nuclei falling into the size range below 0.01 μ . These soils

would appear to be very likely sources of the nuclei that are found in

some precipitation samples.

In summary, the evidence seems to indicate that the high and

variable concentrations of nuclei active at warm temperatures which are

[*] Since cloud conditions are usually not well controlled, the
efficiency of detection can vary and mask some of the real
variations in ice nucleus concentrations.

found in precipitation samples reflect the existence of high concentrations
of nuclei in the air in which the precipitation formed, and that these
high concentrations in the air were not observed previously because of
the inadequacy of instruments for the detection of nuclei effective at
temperatures above -12 C. At temperatures below -15 C, precipitation
samples show less variation in nucleus concentration, which is perhaps
connected with the uniformity of average nucleus concentrations in air
that have been reported. Correlation between ice nucleus concentrations
and the distribution of particulates in general was thought in the past
to be lacking; the model here presented assumes that such correlation
exists at least for nuclei that are active at temperatures above -10 C.
The problem can perhaps be finally resolved when ice nucleus measurements
with improved equipment and the concentrations of particles smaller than
0.01μ size can be obtained simultaneously.

VIII.   ESTIMATED GLACIATING BEHAVIOUR OF CLOUDS

Attention in this chapter will be concentrated on the appearance of the ice phase in convective storms with only cursory mention of other types of precipitation. The picture that emerges from the considerations of the previous chapters for the initial appearance of ice particles in some convective clouds is that high concentrations of potential freezing nuclei are swept up by the updraft, these nuclei are rapidly captured by cloud droplets after condensation has taken place, and in this way frozen cloud droplets are produced. The frozen cloud droplets can be expected to grow fairly rapidly, by the combination of vapour growth and coalescence, developing into larger ice pellets presumably within a few minutes. Only the initial step, the formation of frozen cloud droplets, is considered here quantitatively, the details of their further development being either neglected or bypassed in relating the derived estimates to observations.

The groundwork for the subject of this chapter has been laid in Chapter VI, where the distribution of small particle aerosols and their capture by cloud and raindrops was treated. As shown there, in-cloud scavenging is the most important of the processes that contribute to the freezing nucleus content of precipitation, and the concentrations of freezing nuclei in cloud droplets and raindrops can be taken to be the same as the concentrations measured in the precipitation samples collected at the ground. On this basis, the concentrations of ice particles in the clouds can be estimated from the experimentally determined nucleus spectra.

Nucleus spectra are determined from the freezing temperatures of drops of known sizes, as described in Chapter III. The problem now is the reverse: the calculation of the fractions of various size drops that are frozen at different temperatures, given the measured nucleus spectrum for the bulk water. In accordance with remarks made in Chapter III, the fraction of drops of volume V frozen at temperature θ is

$$f(\theta,V) = 1 - e^{-V \cdot K(\theta)} \tag{1}$$

where $K(\theta)$ is the cumulative concentration of nuclei. (i.e. the number active above θ) This expression is based on the Poisson probability of finding in a drop at least one nucleus of the type whose average number per drop is $V \cdot K(\theta)$. Figure 8-1 shows the relation between drop size, concentration of nuclei and fraction of drops frozen in graphical from. Selected values are also given in table 1.
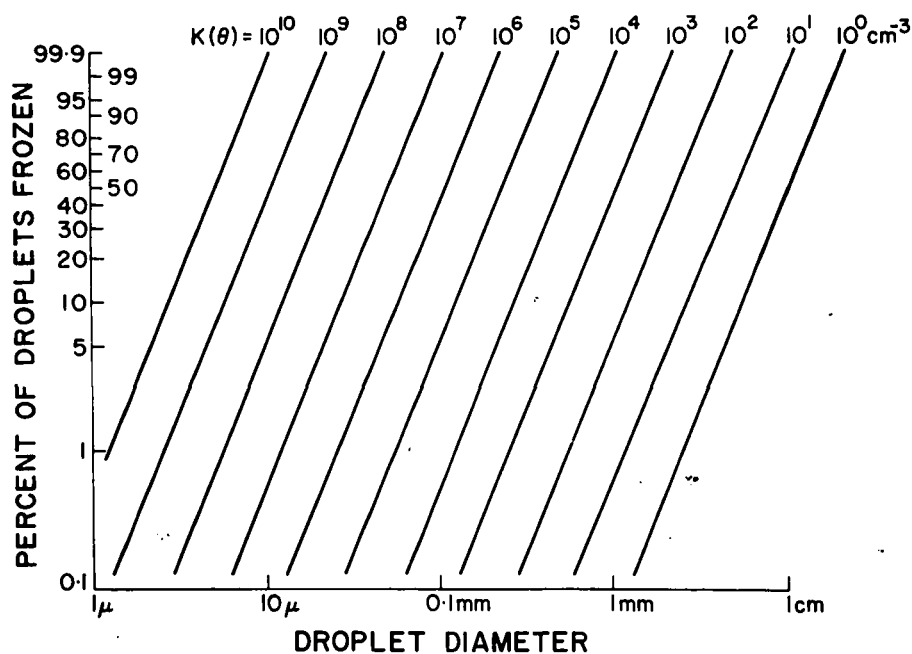

Figure 8-1. Fractions of drops of different sizes frozen at indicated concentrations of freezing nuclei.

TABLE 1

Values of $K(\theta)$ (cm^{-3}) for indicated
drop sizes and fractions frozen

Drop	Fraction Frozen		
Diameter	10%	50%	90%
10 μ	2.0×10^8	1.3×10^9	4.4×10^9
30 μ	7.4×10^6	4.9×10^7	1.6×10^8
100 μ	2.0×10^5	1.3×10^6	4.4×10^6
300 μ	7.4×10^3	4.9×10^4	1.6×10^5
1 mm	2.0×10^2	1.3×10^3	4.4×10^3
3 mm	7.4×10^0	4.9×10^1	1.6×10^2

For polydisperse clouds with drop-size distribution N_D the size
distribution of frozen drops is given by the expression

$$N_D \, f(D,K) = N_D \left(1 - e^{-\frac{\pi}{6} D^3 \cdot K(\theta)} \right) \tag{2}$$

A further quantity of interest is the fraction of condensed water mass
that is frozen at temperature θ. This can be evaluated from the
relation:

$$f(M,K) = \frac{\int N_D \frac{\pi}{6} D^3 \, f(D,K) \, dD}{\int \frac{\pi}{6} D^3 \, N_D \, dD} \tag{3}$$

which is a weighted mean of the frozen fractions of different sizes.

In principle, expressions (1) to (3) contain the answers sought
in this section, but their use is limited by the restricted range of
the $K(\theta)$ - values which can be derived from the experiments. As shown
in Chapter III, the maximum range to which the temperature spectra have
been successfully extended is 10^{-1} cm^{-3} to 10^5 cm^{-3}. Comparison with
Table 1 reveals that these concentrations will suffice to describe the
freezing frequencies in drops of 300 μ diameter or larger. The reason

for this limitation is that the experiments were performed using milli-meter-sized drops and the technique did not lend itself to the use of smaller droplets. For smaller drops, extrapolated values of $K(\theta)$ would have to be used. It is felt that extrapolation of the measured spectra over four or five orders of magnitudes is too uncertain to be useful, but as an inspection of the measured spectra (Chapter V) would indicate, concentrations of 10^8 to 10^9 cm^{-3} would not be reached above -30 C in any case. Thus, appreciable glaciation of cloud droplets cannot be treated successfully by the method developed in this section. The initial appearance of rare ice particles at warmer temperatures will be treated by a different approach later on.

a) __The freezing of raindrops__

For rain, the application of formulas (1) to (3) is straightforward. The required inputs are the measured nucleus spectra and the drop-size distribution. For the latter, the distributions proposed by Marshall and Palmer (1948) were used. These are of the form

$$N_D = 0.08 \, e^{-\alpha D} \quad (cm^{-4}) \tag{4}$$

$$\text{with} \quad \alpha = 41 \cdot R^{-0.21} \tag{5}$$

where R is the rainfall rate in mm hr^{-1} and D is the drop diameter in cm, so that N_D stands for the number of drops per cm^3 of air with diameters within unit interval of D. The number and mass distributions of frozen drops corresponding to a rainfall rate of 3 mm hr^{-1} are shown in Fig. 8-2. Similar distributions, but for R = 100 mm hr^{-1} are shown in Fig. 8-3. In these graphs, the straight lines for the number distri-butions and the outer curves for the mass distributions show the total

(frozen and unfrozen) distributions. The parameter $K(\Theta)$ was given values from 10^{-1} cm^{-3} to 10^4 cm^{-3}; the temperatures that correspond to these concentrations can be found from the measured nucleus spectra for each particular sample. As seen from Figs. 8-2 and 8-3, the maximum number concentrations of frozen drops occur for drops between 0.1 and 0.2 cm diameter, whereas the maximum contribution to the frozen mass comes from drops between 0.2 and 0.4 cm diameter.
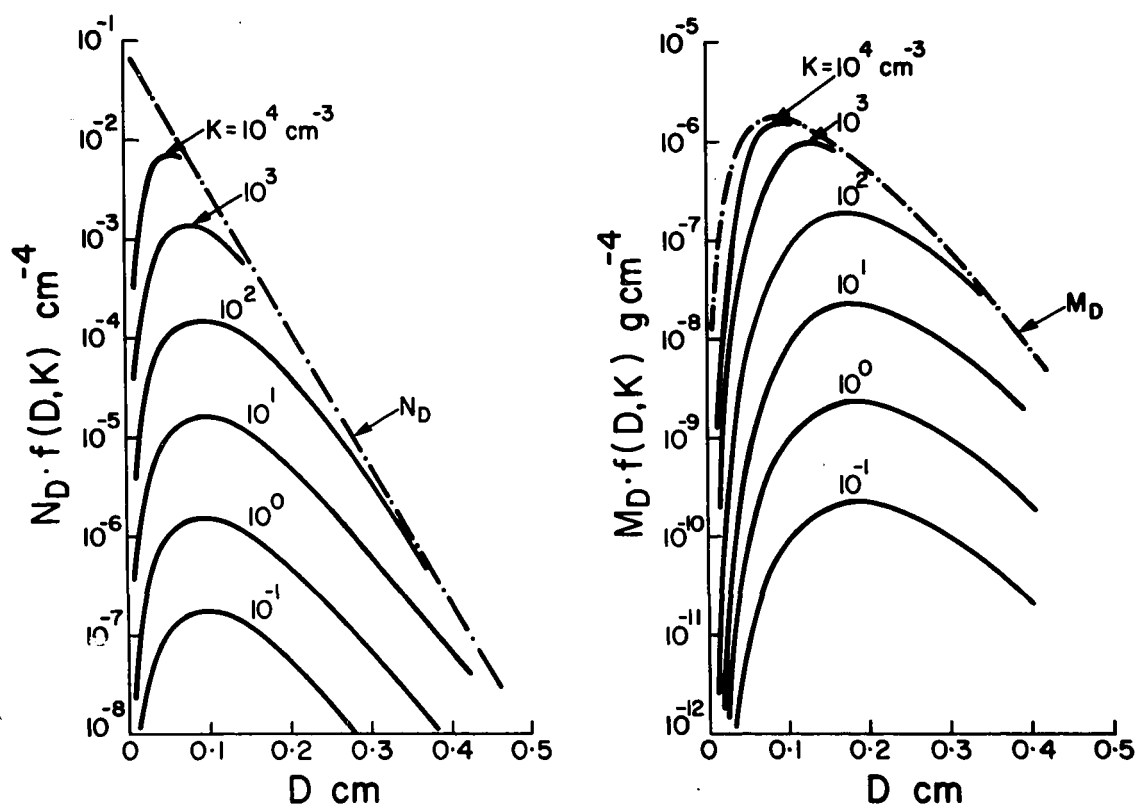
Figure 8-2. Number distribution (left) and mass distribution (right) of frozen drops in 3 mm hr^{-1} rain.
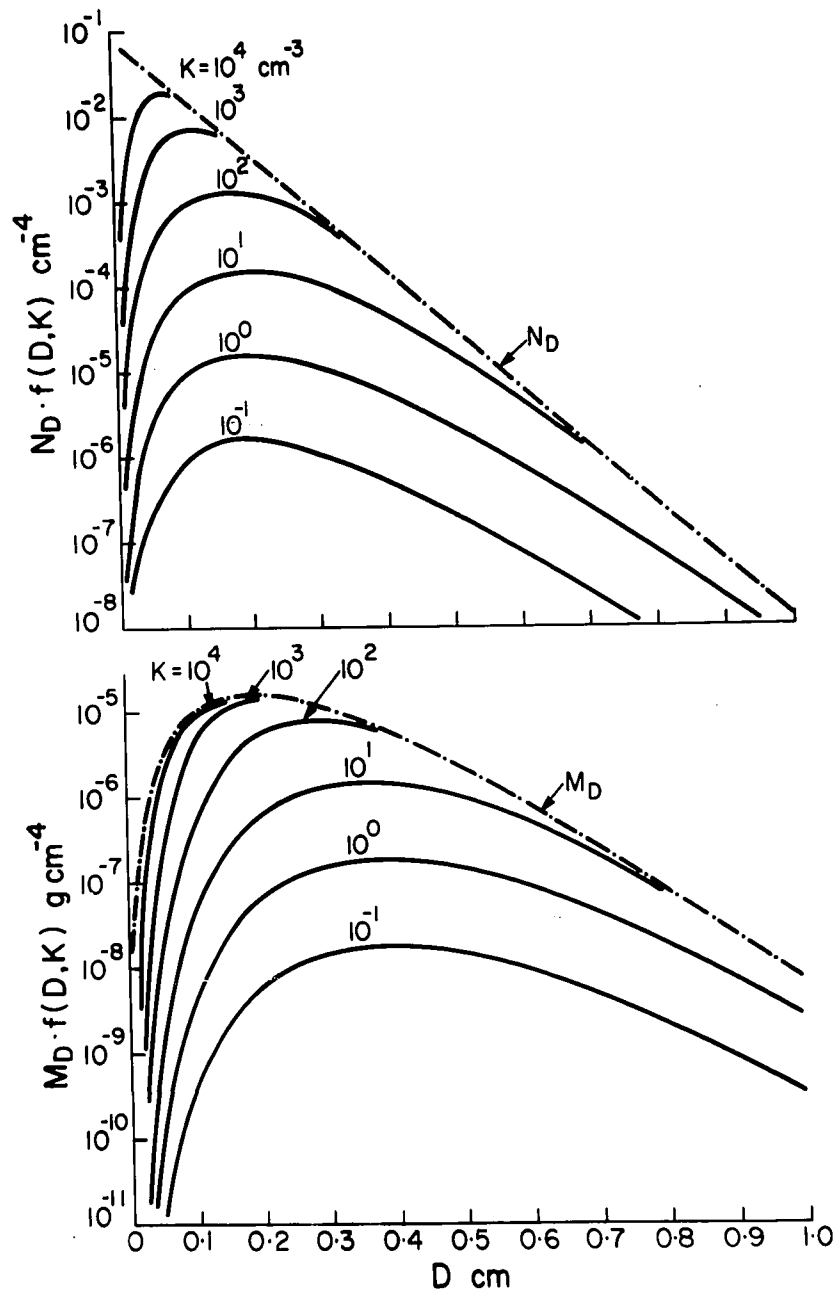
Figure 8-3. Number distribution (above) and mass distribution (below) of frozen drops in 100 mm hr^{-1} rain.
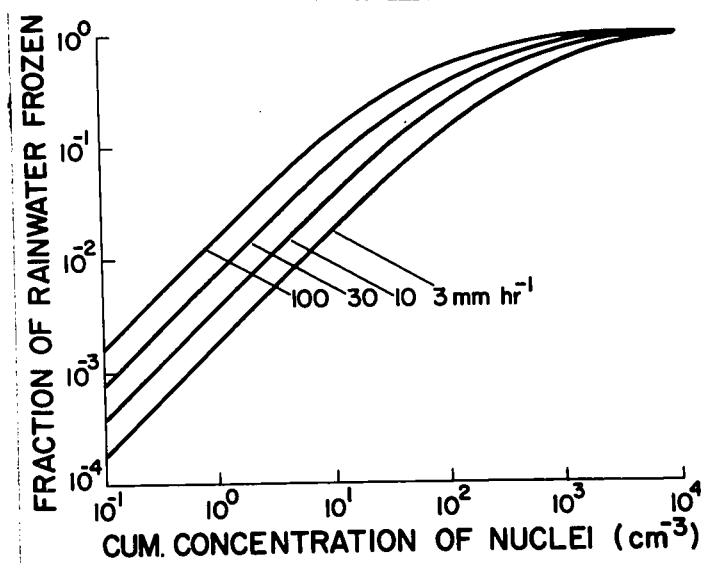
Figure 8-4. Fraction of rainwater frozen as a function of
the concentration of freezing nuclei.

The fractions of total water mass that are expected to be

frozen at different nucleus concentrations (different temperatures)

are shown in Fig. 8-4 for four different values of R. The water

contents corresponding to these rainfall intensities are given in

the table below.

TABLE 2

Liquid Water Content M for
Different Rainfall Rates R

$R(mm\ hr^{-1})$	$M(g\ m^{-3})$
3	0.20
10	0.55
30	1.5
100	4.3

Based on $M \doteq 72\ R^{0.88}$

(Marshall and Palmer, 1948)

At any given nucleus concentration the fraction of water frozen increases with rainfall rate according to Fig. 8-4. This is due to the fact that in the drop size distributions used, the total concentration of drops changes very little, whereas the concentrations of larger drops increase rapidly for higher rainfall rates. Thus, even with the same number of nuclei per cm^3 of water, the fraction of water that is frozen is higher where nuclei have the chance to be found in large drops and therefore contribute heavily to the amount of ice present.

Figure 8-5 shows the fraction of water frozen as a function of temperature for five different nucleus spectra using the size distribution corresponding to $R = 100$ mm hr^{-1}. As shown in the figure, there is a fairly close relation between the shape of the nucleus spectrum and the rate at which the frozen fraction increases with decreasing temperature. The major fraction of the water content can be seen to freeze in a temperature interval which varies from about 2 deg to 10 deg for the different samples.

The use to which information such as that presented in Fig. 8-5 can be put is illustrated by the influence that the relative proportions of supercooled water and of ice have on the growth of hailstones. Fig. 8-6 shows three different curves for the fractions of rain frozen and three hail trajectories that were computed for identical conditions except for the nucleus content of the rainwater. The model on which the calculation of the hail trajectories was based was described by English (1966). As Fig. 8-6 shows, the ultimate size of the hailstone is not influenced greatly, this being dependent mostly on the updraft velocities, but there are major differences in the amount of unfrozen
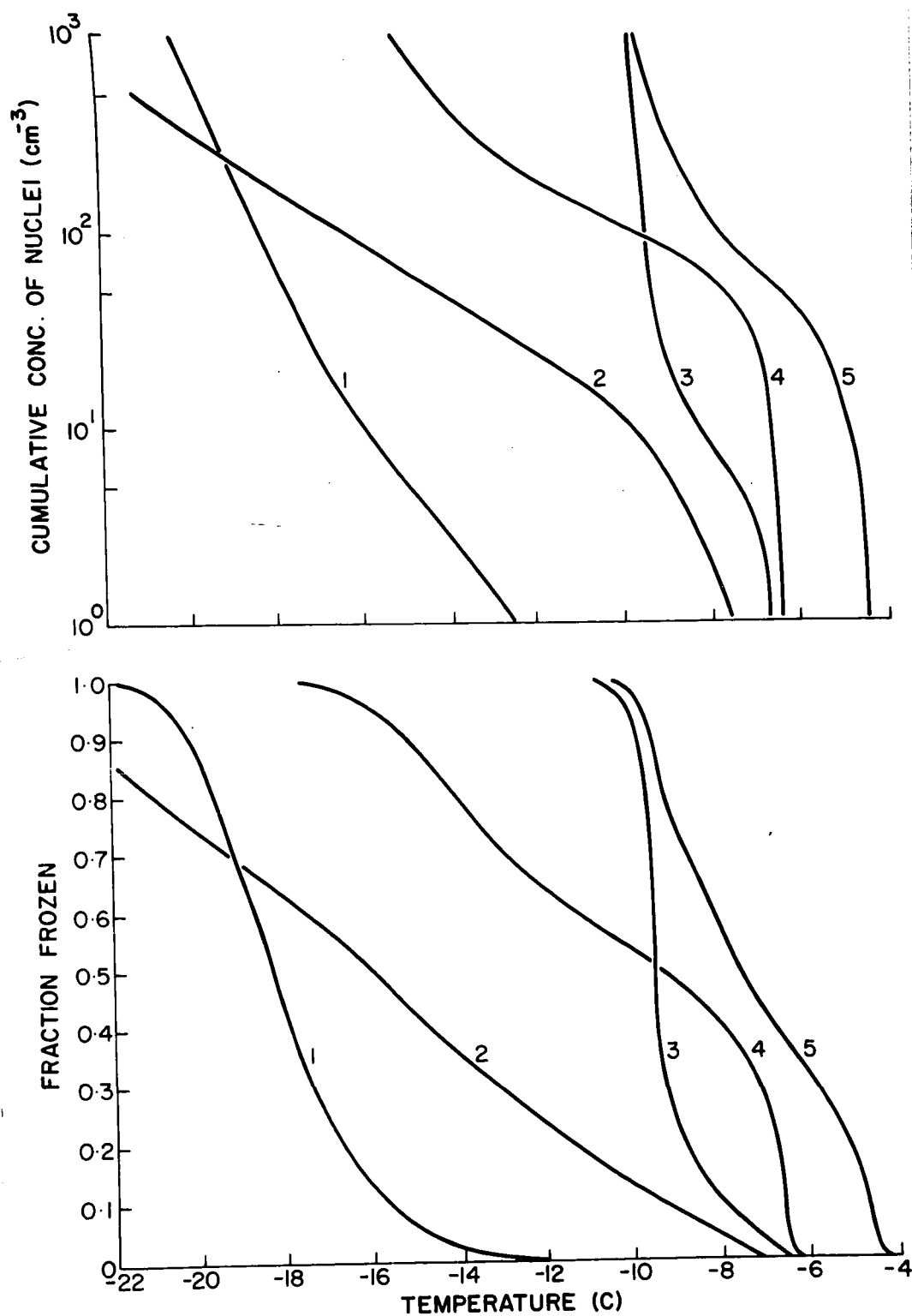
Figure 8-5. Cumulative nucleus spectra (above) and
corresponding fractions of rainwater frozen (below)
for five different hail samples.

water in the stones at the end of their trajectories. For trajectory 1 the resulting hailstone would be 40% liquid, for trajectories 2 and 3 the unfrozen water content would be 20% and 10% respectively. High nucleus content and corresponding early freezing of the rainwater are thus seen to reduce the wetness of the model hailstones.

The method described and used above is quite generally applicable and could prove to be useful in modelling a variety of cloud physical processes. The size distribution of drops was assumed to be known in the foregoing, and also it was taken to be invariant with time while in reality the size distributions change continually and the onset of

Figure 8-6. Hail growth (right) for different degrees of glaciation of the ambient rainwater (left). The growth curves show the diameter of the growing stone at different positions along its up and down path in the cloud. Arrows indicate the points at which the hail growth changes from "dry" to "wet".

freezing will affect the development too. However, these interactions can perhaps be considered secondary, in which case the results presented here should be reasonably good approximations.

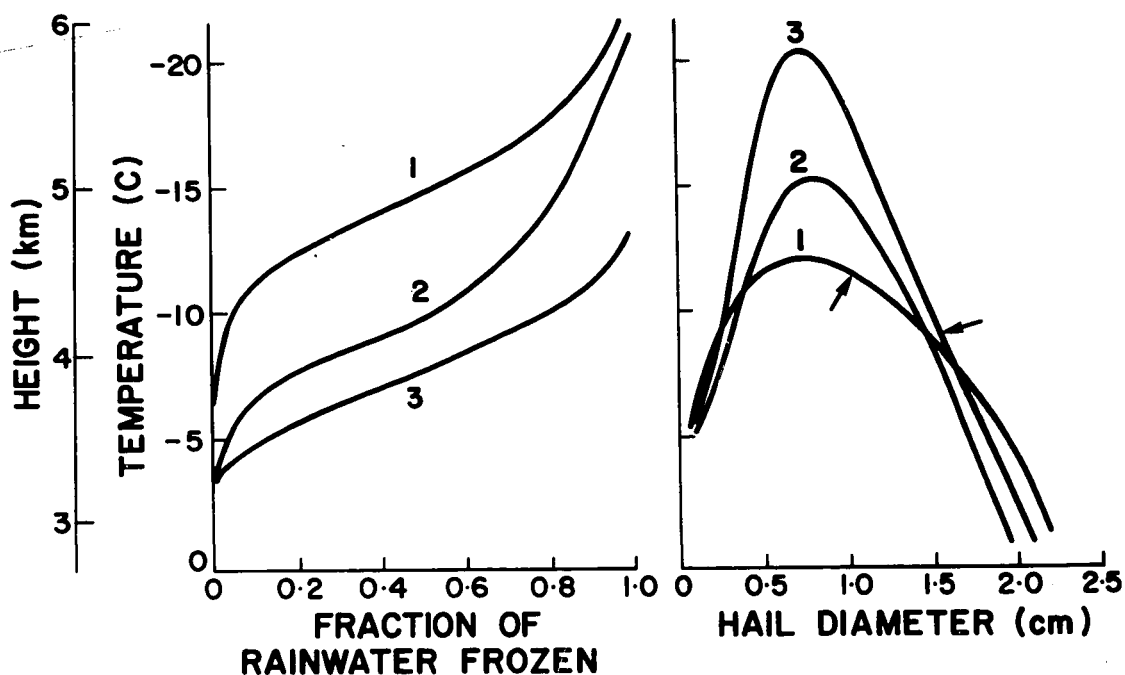b) The formation of ice in clouds

Returning now to the problem of the first appearance of ice in a fresh cloud, at temperatures around -10 C, a method different from that used for rain is needed. As mentioned earlier, appreciable fractions of cloud droplets which are less than about 100μ in diameter are not expected to freeze above -30 C. At warmer temperatures the same cloud will have a very small fraction of its droplets frozen, but due to the abundance of droplets, the number of frozen droplets may still be significant for consideration of hail initiation and growth and indeed for the development of precipitation in general.

Instead of considering the probability of finding a nucleus in a given drop as was done for raindrops, it will now be simpler to use the assumption that the number of nuclei that become active above some temperature θ in a given volume of water is independent of how the water is dispersed. If the water is dispersed into very small droplets, then there is a one-to-one correspondence between number of nuclei and number of frozen droplets. Therefore, to estimate the volume concentration of ice particles in the air, it is only necessary to know the amount of water present in a given volume of air and the concentration of nuclei per cm^3 of water. Since in this way the actual manner of dispersal, the size distribution, is not considered, one estimates the number of ice particles irrespective of size.

It should be pointed out at this point that for the initial
appearance of ice particles in a cloud, the probability for a given
cloud droplet to be frozen is not proportional to its volume, as is
the case for raindrops. Since the assumed process for the collection
of ice nuclei is diffusive capture from the air by the cloud droplets,
the probability for the freezing of a cloud droplet is determined by
the probability for the droplet to capture an ice nucleus, which
varies linearly with droplet diameter. For the small range of drop-
let diameters involved, this variation is probably negligible, so
that almost no size-dependence exists for the first appearance of
frozen cloud droplets. Once frozen, however, the droplets will grow
more rapidly, so that if an observation is made, the ice particles
are likely to be found larger than the supercooled drops; but this
is a consequence and not the cause of these drops being frozen.

It was shown in Chapter VI that the concentrations of nuclei in
precipitation samples represent reasonable first approximations to the
nucleus contents of the clouds from which the precipitation developed.
On this basis, the cumulative nucleus spectrum for a precipitation
sample may be interpreted as a relation between temperature and the
number of ice particles that develop in the cloud within the volume
of air in which 1 g of cloud water is dispersed. With known or
assumed values of the liquid water content of the cloud, the concentra-
tions of ice particles per m^3 of air can then be obtained. Figure 8-7
shows two sets of curves, one typical of hail and one of rain, giving
the concentrations of ice particles for assumed liquid water contents
of 0.5 to 4 gm^{-3}. Taking 2 gm^{-3} as an average value for the liquid
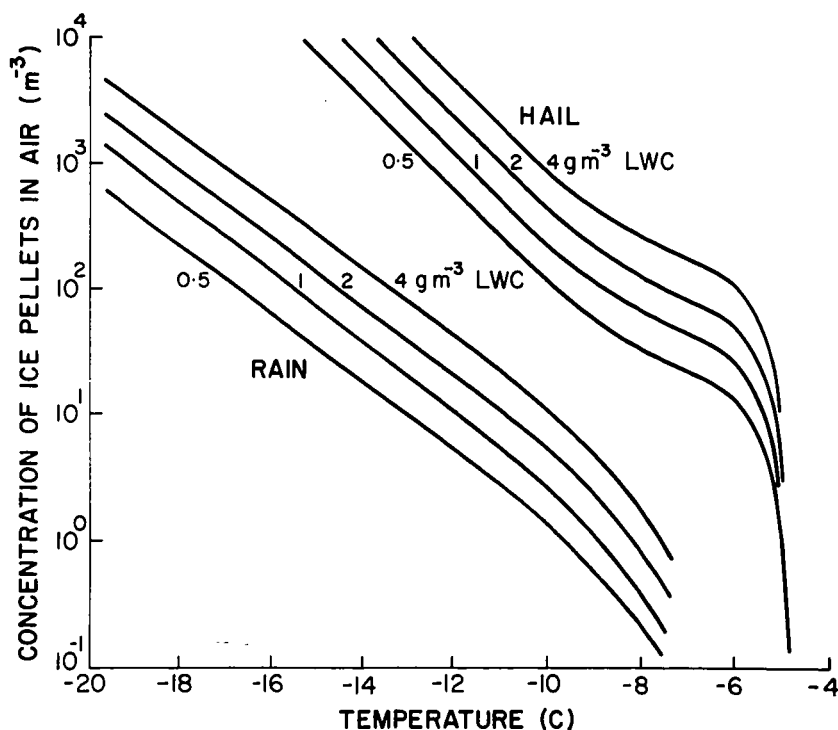
Figure 8-7. Estimated concentrations of frozen cloud
droplets for two typical nucleus spectra and with
different values assumed for the liquid water contents
of the clouds.

water contents of a convective cloud, Fig. 8-7 indicates that if the

sample represented by the "hail" curve had indeed come from a cloud

with such liquid water content, then ice pellet concentrations of

10^3 m^{-3} may have been reached at -10 C in that cloud.

Braham (1965), in summarizing the findings of Project Whitetop,

reported that about 1/3 of summer clouds in Missouri develop snow

pellets or graupel if the cloud tops reach -10 C, and that pellet

concentrations of 10^3 to 10^4 m^{-3} were frequent in clouds whose top

was at or below -10 C. He further reported that most pellets appeared

to be rimed cloud droplets. These observations are in good agreement

with the predictions of the previous paragraphs, although the applica-

bility of the nucleus spectrum used to clouds in Missouri remains

hypothetical. Similar recent observations were reported by MacCready et al. (1965) and by Mossop et al. (1967).

The dilemma caused by the apparent contradiction of observations such as Braham's with the ice nucleus concentrations that are measured at temperatures around -10 C in cloud chambers has been a major source of debate regarding the glaciation mechanisms of clouds (Koenig, 1965, for example). It appears from the foregoing that freezing of cloud droplets may well be the generating mechanism for the ice particles at warm temperatures, provided that the high aerosol concentrations postulated and the time required for capture of the nuclei by the cloud droplets are available.

As pointed out earlier, the experimental information on the concentrations of freezing nuclei has its greatest importance for the prediction of the initial formation of the ice in a cloud at temperatures above -10 C or perhaps -15 C, and for the estimation of the relative proportions of frozen and supercooled rainwater in clouds. These are of particular relevance for the development of hail, the former as its starting point and the latter as the environment in which the hail grows, but the formation of ice pellets at warm temperatures may also influence the rain-generation processes.

IX.   THE FREEZING NUCLEUS BUDGET OF STORMS

The water budget of storms has been investigated by several
workers and the efficiency of storms, that is the ratio of the mass
of precipitation to the mass of water vapour input, estimated as
from 10% to 50% for storms of various sizes. For a hailstorm,
Newton (1966) estimated that the influx of water at the base of the
storm is 8.8 kton sec^{-1} or 8.8 x 10^9 g sec^{-1} and that the precipitation
reaching the ground is 4 x 10^9 g sec^{-1}. These estimates were given for
the type of storm that occurs on the central plains of the United
States; Chisholm (private communication) estimates that even though
Alberta hailstorms, being somewhat smaller and developing in a drier
environment, may have input and output rates from 1/4 to 1/2 as great
as those given by Newton, their efficiencies are comparable or perhaps
even higher. Fifty percent may thus be taken as a representative value
for the efficiency of hailstorms at their mature stage. Holtz (1968)
has shown that the efficiency of a large storm varies with time: from
10% at the time high concentrations of precipitation inside the storm
begin to develop to 50% at the peak intensity of the storm. Ten to
fifty percent thus represents the range of efficiencies for storms of
different sizes, as well as the range of variation with time of the
efficiency of a large storm.

Given the water vapour content of the air feeding the storm, the
figures for the water budget can be converted to an estimate of the
volume of air from which a given amount of precipitation develops. The
nucleus content of the input air can then be calculated from the nucleus

content of the precipitation, on the assumption that the precipitation
contains all the nuclei that enter the storm. With capture of nuclei
by cloud droplets as the scavenging mechanism, almost total transfer
of nuclei from the air to cloud can be expected, and since droplets
that freeze at relatively warm temperatures have the best chance for
developing into precipitation, the precipitation will contain the
majority of active freezing nuclei that were in the air. This argument
might not be valid if the concentrations of active nuclei are high so
that not all frozen cloud droplets can grow large enough to precipitate.

The ranges of concentrations of nuclei in precipitation are given
in Table 1 for temperatures of -6 C, -10 C and -14 C. These data are
taken from results presented in Chapter V.

Table 1

CUMULATIVE CONCENTRATIONS OF FREEZING
NUCLEI IN PRECIPITATION (cm^{-3})

	LOW	HIGH
-6 C	1×10^{0}	4×10^{1}
-10 C	6×10^{0}	1×10^{3}
-14 C	3×10^{1}	2×10^{4}

The number of nuclei that would be required per unit volume of air
to account for these observed concentrations in the precipitation
are given in Table 2 for different values of storm efficiencies and
water vapour contents of the air. The different combinations of storm
efficiencies and water contents account for at most a tenfold variation

Table 2

CONCENTRATIONS OF NUCLEI IN AIR ENTERING STORM

TEMPERATURE (C)	STORM EFFICIENCY (%)	WATER CONTENT OF AIR ($g\ m^{-3}$)	CONCENTRATION OF NUCLEI (m^{-3})	
			LOW	HIGH
-6	10	5	5×10^{-1}	2×10^{1}
		10	1×10^{0}	4×10^{1}
	50	5	2×10^{0}	1×10^{2}
		10	5×10^{0}	2×10^{2}
-10	10	5	3×10^{0}	5×10^{2}
		10	6×10^{0}	1×10^{3}
	50	5	1×10^{1}	2×10^{3}
		10	3×10^{1}	5×10^{3}
-14	10	5	1×10^{1}	1×10^{4}
		10	3×10^{1}	2×10^{4}
	50	5	6×10^{1}	4×10^{4}
		10	2×10^{2}	1×10^{5}

Note: Water content and nucleus concentration are given for unit volume of air at the surface.

in the nucleus content. This is smaller than the ratio of the "low"
and "high" concentrations, indicating that the large differences in
nucleus content among precipitation samples are caused mainly by differ-
ences in the nucleus content of the air entering the storm.

The nucleus concentrations given in Table 2 are plotted in Fig. 9-1
as vertical bars, labelled H and L for the "high" and "low" values
respectively. Also shown on this graph are some nucleus spectra obtained
by other workers from cloud chamber measurements. Curves 1, 2, 3 and 4
represent the highest concentrations reported by Smith and Heffernan
(1954), Isono (1965), Rau (1954) and Bigg (1961) respectively. Curve 5
represents the average of about 30 observations by Bourquard (1963);
individual spectra differ by about ±1 deg from the average. Curve 6 is
reported by Bigg (1965) as the concentration that is representative of
average conditions at many widely differing places. The range of concen-
trations between curves 5 and 6 is generally believed to represent
typical atmospheric conditions. As shown by Fig. 9-1, the agreement
between "high" estimates and the extreme concentrations, and between "low"
estimates and typical concentrations, is fairly good at temperatures colder
than -10 C. At warmer temperatures, cloud chambers do not have sufficient
sensitivity to measure the atmospheric concentrations of nuclei (cf.
Chapter VII). The points that should be emphasized are (i) the concen-
trations of nuclei derived from measurements on the precipitation are in
most cases higher than the generally accepted typical atmospheric concen-
trations, and (ii) a nucleus concentration of 10^2 m^{-3} may be reached in
some cases at temperatures as warm as -6 C, whereas the same concentration
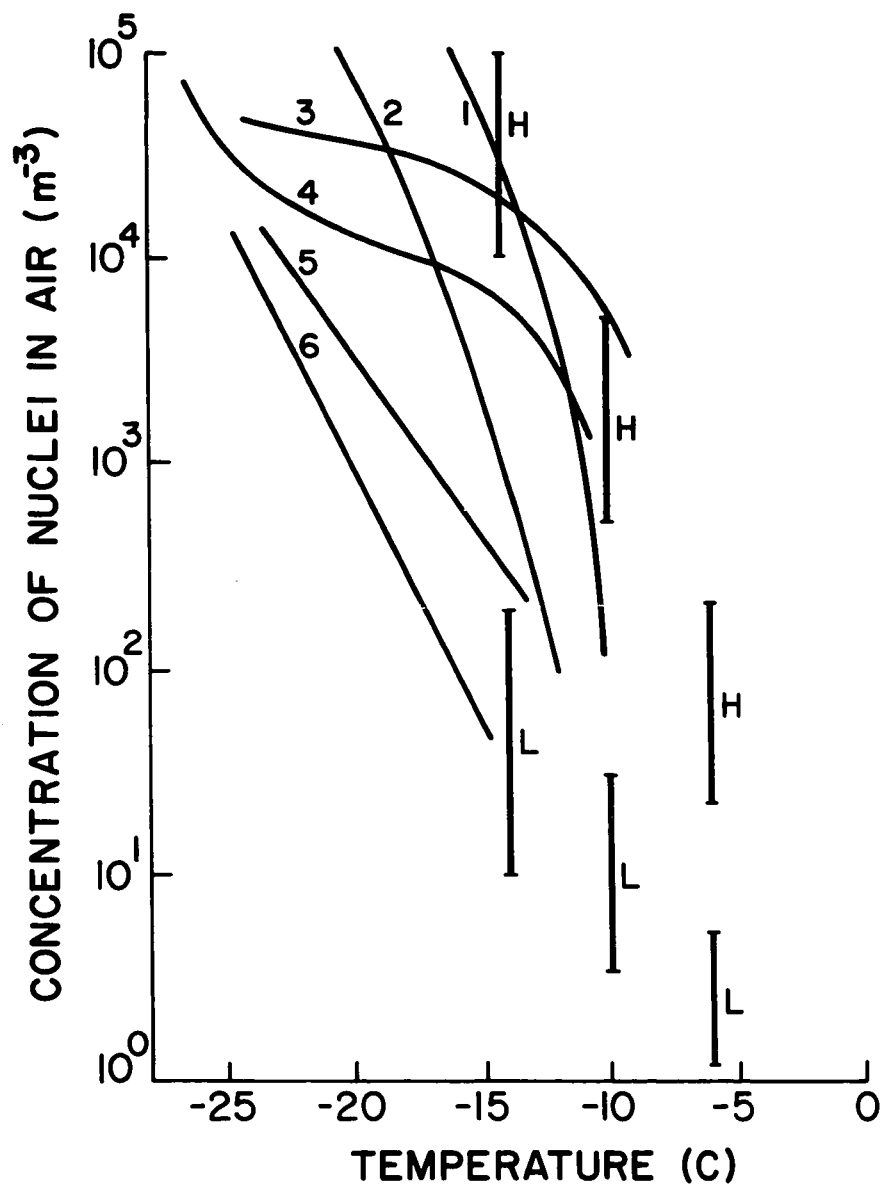is reached in most cloud chamber measurements only at -15 C.

Figure 9-1.   Estimated and measured concentrations of freezing nuclei in air. Vertical bars are estimated concentrations from Table 2. Measured concentrations: 1 - Smith and Heffernan (1954); 2 - Isono (1965); 3 - Rau (1954); 4 - Bigg (1961); 5 - Bourquard (1963); 6 - Bigg (1965).

From the estimated nucleus concentrations and storm inflow rates, the rates at which nuclei enter a storm can readily be obtained. Newton (1966) gave a value of 7×10^8 m^3 sec^{-1} as the rate of air intake by a storm. For Alberta hailstorms updraft areas of 50 km^2 and updraft speeds of about 5 m sec^{-1} may be taken as typical, giving 3×10^8 m^3 sec^{-1} as the air influx. The flux of nuclei into the storm can therefore be estimated as well as the total numbers of nuclei that enter a storm during its lifetime; figures are given in Table 3 for a typical Alberta hailstorm of 3 hr duration, and for the "high" concentrations from Table 2.

Table 3

FLUX AND TOTAL NUCLEUS INTAKE
FOR HAILSTORM

TEMPERATURE (C)	FLUX (sec^{-1})	TOTAL
-6	6×10^{10}	6×10^{14}
-10	2×10^{12}	2×10^{16}
-14	3×10^{13}	3×10^{17}

The figures in Table 3 could have been obtained directly as the amount of precipitation produced by the storm times the concentration of nuclei in the storm. An average rainfall rate of 50 mm hr^{-1} over a 100 km^2 area corresponds to 10^9 g sec^{-1} precipitation or 10^{13} g over the life of the storm. Combining these figures with the concentrations given in Table 2 yields values for the flux and total intake which agree with those given in Table 3.

The concept of cloud seeding for hail modification is to increase
the concentrations of ice nuclei in the clouds by one or perhaps two
orders of magnitude over the naturally-occurring concentrations. The
estimates given above for the number of natural nuclei that enter a
hailstorm can serve to indicate the fluxes of artificial nuclei that
would be needed to achieve such increases in concentration. According
to Fukuta (1967) the outputs of airborne generators of silver iodide
nuclei are about 10^9 nuclei per second for activity at -6 C and 10^{11} to
10^{12} sec^{-1} for activity at -10 C. The output of a generator of metal-
dehyde nuclei is reported by Fukuta (loc. cit.) as 2×10^{12} sec^{-1} and
3×10^{13} sec^{-1} for nuclei active at -6 C and -10 C respectively.
Comparing these figures to the estimated fluxes of natural nuclei given
in Table 3, it is seen that the outputs of present-day silver iodide
nucleus generators fall short of even equalling the natural flux of
nuclei into a large hailstorm. The metaldehyde generator provides a
six to tenfold increase over the natural flux. Such a direct comparison
of natural flux and generator outputs assumes that the entire output of
artificial nuclei from the generator is delivered to the core of the
storm, and that the cloud chamber measurements, from which the quoted
outputs are derived, are representative of the effectiveness of the nuclei
in a natural cloud. The degree of correspondence that can be expected
between the laboratory and natural conditions in this respect depends on
the mode of action of the nuclei (sublimation or freezing), on how the
nuclei are captured by cloud droplets (for freezing nuclei) and on the
rate of deactivation of the nuclei with time, but the behaviour of silver
iodide, metaldehyde and other nucleating substances in these respects is
not well known at present.

The nucleus concentrations inside storms and the rates of inflow of nuclei into the storm were estimated in the foregoing from the concentrations of nuclei in the precipitation. These estimates were obtained without consideration of the details of the precipitation process. However, it was shown in Chapters VI and VII that natural freezing nuclei, large fractions of which are smaller than $0.01\,\mu$ diameter, are captured efficiently by cloud droplets, and therefore the nucleus concentrations derived in this chapter represent with reasonable accuracy the concentrations that occur in clouds. The results may be said to be more realistic than the information presently available by other means in that ice nucleus measurements inside active storms have not been obtained so far and the measurements that have been made, at the ground or near storms, were made with cloud chambers which are inefficient for the detection of nuclei active at temperatures warmer than -10 C.

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