CLOUD CHAMBER STUDY OF WATER EVAPORATION

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ABSTRACT

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A cloud chamber system was developed to study the evaporation of water and a series of experiments performed to demonstrate its ability to carry out such investigations. An analytic method was developed to interpret the results of the study and a relationship between evaporation resistance and water surface tension established. The effect on evaporation of long-chain alcohol monolayers was examined and Tetra, Hexa, and Octadecanol alcohols found to be better inhibitors than Dodecanol. Two particularly important applications of the cloud chamber system developed: the study of the effect of dissolved contaminants on evaporation resistance of water and the effect of surface barriers on the evaporation rate. NaCl inhibits evaporation strongly with the resistance to evaporation increasing with the concentration of salt in solution. CaCl apparently reduced the resistance to evaporation. The development of a cloud within the chamber as a function of chamber atmosphere temperature gradient showed a fog-like behavior for gradients greater than 1°C/cm. For smaller gradients the cloud development was generally uniform throughout the chamber. Cloud development as a function of water temperature was observed and a variation in evaporation resistance noted.

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I. INTRODUCTION

This report constitutes a summary of the work done on the New Mexico Water Resources Research Institute Project No. A-024; 3109-35. The project entitled "A Cloud Chamber Study of Water Evaporation" was funded from September 1969 to July 1972 and consisted of the development of a cloud chamber and the construction of associated control and data collecting devices, an investigation of the effect of various physical parameters and substances on evaporation from a liquid water base, and the development of techniques of analysis. Not all parts of the project were carried to completion and some of those completed could not be interpreted in a meaningful way. However, a system was developed which is capable of studying water evaporation and the results are presented here. Due to the increased administrative responsibility of the principal investigator and the corresponding decrease in time available to devote to this project, no additional funding was requested to complete the program. This work will continue to proceed at a slower pace and be supported by the Department of Physics to its conclusion.

A. Technical Discussion

Attempts to reduce the rate of evaporation of water from ponds, lakes, and streams have been a matter of worldwide concern for many years, and many and varied experiments have been performed in the laboratory and in the field. A general summation of studies on evapo-

ration of water is presented in a monograph by J. Frenkiel, and Magin and Randall² give an extensive review of the literature on evaporation suppression. Most of the experiments reported in the literature have been aimed at testing the effect of a particular method of evaporation reduction and have not successfully established either empirical or theoretical relationships between the environmental parameters, the rate of evaporation from the body of the liquid, and the physical properties of the liquid or its surface. Many laboratory experiments have failed to account for the multitude of variables present in the field and field experiments suffer from the large number of uncontrolled variables generally present. Wind, wave action, dust contamination, and temperature become factors over which the experimentalist has no effective control. An on-site experiment is, of course, the ultimate experiment which must be performed for the final evaluation of any evaporation retardation technique proposed; however, a laboratory experiment to deduce the relationships between certain parameters and the evaporation process under very carefully controlled conditions would be valuable. Such an experiment was conducted under the auspices of this program by using an expansion cloud chamber and applying it to the study of water evaporation and the problem of evaporation reduction.

The cloud chamber has not been applied previously to a study directed toward the examination of the evaporation of bulk water as a function of various environmental factors. It has primarily been used as a tool for the study of atomic and sub-atomic particles, the

purpose for which it was originally designed. Recently, however, the cloud chamber has been used by Kassner and his co-workers 3-6. Lund and Rivers 7 , and Schuster and Good^8 as a means of studying the nucleation and the growth and evaporation of liquid drops of water and to establish the drop size distribution in clouds. Its use is based on the fact that it is possible to supersaturate the chamber volume by expansion and cause the growth of drops on whatever nucleation centers are present. One can adjust the chamber so that growth will take place only on the vapor molecules (homogeneous nucleation) and not on ions or neutrals of another species (heterogeneous nucleation). Thus, a cloud can be generated which is formed by vapor condensation on water vapor molecules only and changes observed in the cloud formation as a function of the variation of a given parameter. The cloud formed is a measure of the water vapor content of the chamber atmosphere and therefore a measure of the cloud density and can be related to the evaporation taking place in the chamber. Variations in such parameters as pressure, temperature, atmospheric composition, liquid surface tension, specific gravity, electric field strength, etc., can be related to evaporation through changes in the cloud density, and the effect on evaporation of surface barriers, dissolved contaminants, etc., can be observed in the same manner.

Cloud density determinations in Wilson cloud chambers are generally carried out by counting droplets in a cloud photograph , by estimating the droplet concentration , or by relying on a criterion of "critical supersaturation" 10. In the present experiment a technique developed by

Schuster¹¹ was used to determine the cloud density. This technique utilized measurements of scattered radiation from a helium-neon laser beam (6328 Å) which was incident on the cloud to determine an average droplet concentration for a given chamber condition.

B. Principle of Operation of the Chamber

The operation of a cloud chamber resulting in cloud formation can be briefly described by considering a volume of gas that is saturated with a condensable vapor and the existence of a mechanism for suddenly cooling the system. When cooling occurs, the water vapor that is excess at the lower temperature separates out in the form of droplets until vapor equilibrium of the system is established at the lower temperature. If the chamber is cooled by expansion at the proper rate and extent, then the necessary supersaturation is established for molecules of water in the chamber atmosphere to serve as centers of condensation for the vapor. A cloud will form.

The supersaturation S required to attain the desired condition for homogeneous nucleation can be expressed in terms of the chamber parameters as the ratio of the vapor density prior to condensation but after expansion, ρ_f^i , to the density of the equilibrium system at the final temperature, ρ_f . Using this definition and the condition that the chamber expansion is adiabatic, one can express the supersaturation in the usual form given by

$$S = \frac{\rho_f'}{\rho_f} = \frac{P_i}{P_f} \left(\frac{1}{1+\epsilon}\right)^{\gamma}$$

where P_{i} and P_{f} refer to the vapor pressure at equilibrium before and

after expansion respectively, $1/(1+\epsilon) = V_f/V_i$ is the expansion ratio expressed as the ratio of initial and final volumes, and γ is the ratio of specific heats of the gas-vapor mixture in the chamber. The method employed for actually calculating the supersaturation was a slight variation from the above relationship as recommended by Kassner and Schmitt⁵. The details are presented in that report and by Loftin¹². A complete theoretical and general discussion of cloud chambers is presented in the classic paper of Das Gupta and Ghosh¹³.

C. Project Objectives

The project objectives as stated in the original proposal are summarized as follows:

- (1) To develop the cloud chamber as a tool for the examination of parameters important to the study of evaporation of water.
- (2) To investigate the rate of evaporation of pure water as a function of various parameters.
- (3) To establish a quantitative relationship between the evaporation rate and the various parameters.

The degree to which the various objectives were met can be stated briefly as follows:

Objective 1. This objective was realized nearly in its entirety and resulted in the design and construction of an extremely versatile Wilson-type cloud chamber. The chamber is capable of establishing fine temperature and pressure control over a wide range of values and is constructed so that substances may be easily introduced into the system for the study of the effect of contaminants on evaporation. During the

development two cloud chambers were actually designed and constructed, the first being a redesign of an already existing chamber for use during the preliminary investigations, the second being a newly designed and constructed chamber for the evaporation studies. The design and construction of each of these, along with the accompanying control devices and preliminary studies, are reported in detail by Dodge 14.

Objective 2. The second objective was altered so that the investigation was not concerned with the "rate" of evaporation but with the extent to which evaporation took place in a given time interval. This change in approach was made due to the fact that the time to approximate equilibrium between the liquid and its vapor was generally much shorter than the time to establish the thermodynamic equilibrium necessary to the operation of the chamber. The fact that simple rate measurements could not be employed greatly complicated the use of the chamber for this study. However, a method of analysis was developed which permitted the cloud densities observed under equilibrium conditions to be used as a qualitative measure of the evaporation. The method is presented in detail in this report. Not all substances or parameter variations initially included in the plans for this study have been investigated, and some of the experiments performed should be redone. These will be included in the continuation of the program.

Objective 3. This objective has not been attained at this time. It was pointed out in the original proposal that it would probably not be attainable during the first three years and that estimate was correct. We display data yielding relationships between certain parameters and

evaporation and some qualitative explanations for the effect of some of these parameters on evaporation, but have not as yet developed a quantitative theory to explain the observed results. It is believed that eventually, for example, those cloud density data presented as a function of surface tension can be related through theory directly to the diffusion process controlling the movement of water molecules through the surface of the liquid.

II. APPARATUS

This study required the development of a special cloud chamber and associated control equipment in order to have the versatility necessary to examine various parameters for their effect on evaporation. Actually, two cloud chambers were used; a chamber previously used in this laboratory for a drop-size distribution investigation 11, and a chamber specifically designed to examine the evaporation process. The former chamber was used in this study to examine certain operating relationships which were needed to proceed with the design of the new chamber and also to evaluate the control system and associated devices. It is described completely by Dodge 14 and will not be discussed further in this report. The new chamber, which was used to collect the data for this experiment, is also discussed by Dodge but the description given here will be that presented by Loftin 12 which incorporates some recent alterations.

A. The Chamber Proper

The chamber was constructed of a one-third inch thick glass cylinder approximately six inches in height and five and one-half inches inside diameter. Feed-throughs were provided in the removable, non-magnetic stainless steel top for water inlet, gas inlet and outlet, clearing field, pressure transducer and thermocouple probes. A window was also provided in the center of the top for photographic purposes. The clearing field anode was a circular copper disk with a hole cut in the center so as not to obstruct the window. The clearing field disk

was affixed to the inside of the top via insulating standoffs. A nominal clearing field of 100 volts/cm was used. Wrapped around the glass cylinder were two turns of nichrome heating wire used to warm the chamber walls to prevent condensation. The bottom of the chamber was a rubber diaphragm immediately below which was an air actuated piston assembly. Figure 1 provides a cross-section of the chamber and piston assembly. Figure 2 shows a top view of the chamber and associated components, and Figure 3 a photograph of the assembly. To facilitate access to the chamber and arrangement of peripheral equipment, the chamber was mounted in the center of a two-by-four foot table.

B. Piston Assembly

Compression and expansion was accomplished by a compressed air operated piston which positioned the rubber diaphragm. To drive the piston, an electric valve assembly was designed to regulate air flow to the piston. A nominal main line pressure of 65 p.s.i. was used to pressurize a manifold which was connected to the piston through the electric valve assembly. The valve assembly is shown in Figure 1. To compress the chamber, V1 and V3 open to allow pressure to the bottom of the piston and the top to exhaust. To expand the chamber, V1 and V3 close, V2 and V4 open to allow pressure to the top of the piston and the bottom to exhaust through a rate control valve V5. All electric valves were designed for continuous duty and were activated by a programming circuit. Piston stroke was limited to two inches. An exhaust rate of 8.33 in/sec had been previously determined to be an optimum rate for cloud formation. The total expansion time was 0.24 sec.

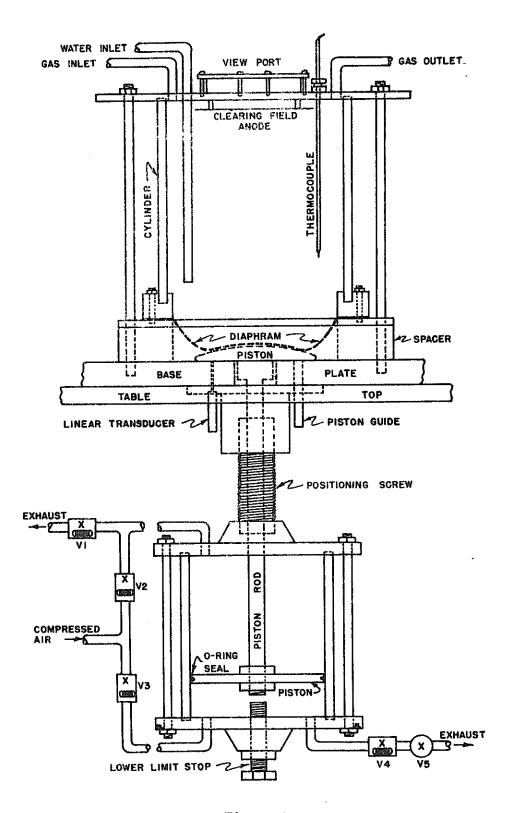


Figure 1
Chamber and Piston Assembly Cross-Section

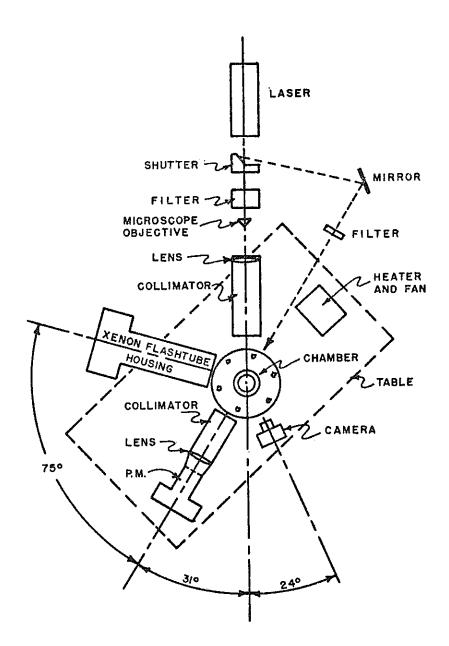


Figure 2
Chamber System, Top View

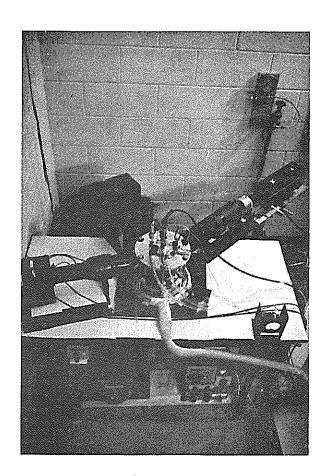


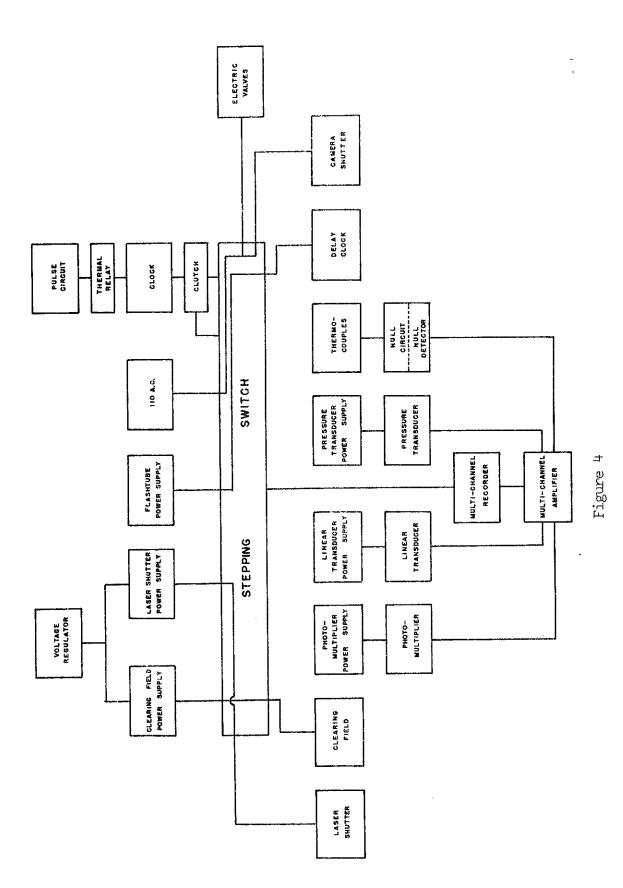
Figure 3
Photograph of the Cloud Chamber Assembly

C. Programming

As it is absolutely essential that the chamber cycle in an exactly reproducible manner, all chamber functions were controlled through an electronically pulsed twenty circuit stepping switch. Figure 4 is a block diagram of the system indicating the functions controlled through the stepping switch. The stepping switch itself was activated from a delay timer to control chamber dead time, which was set to the optimum value of four minutes.

D. Photoelectric System

Scattering of coherent light from the cloud was used to determine the cloud density. A one milliwatt helium-neon laser (6328 Å), was used as the coherent source. Diverged through a microscope objective and collimated, the beam was passed through a 2 x 7 cm slit, whereupon it entered the chamber. The beam filled the chamber from clearing field anode to water surface. Light scattered from the beam was detected by a collimated ten stage photomultiplier (Dumont KM2433). The photomultiplier signal, being proportional to the cloud density, was recorded. To prevent the beam from entering the chamber directly when an expansion was not occuring, a rotating shutter was placed between the laser and the microscope objective. When the shutter was closed it deflected the beam to a mirror and filter arrangement which in turn deflected it to the photomultiplier through a sheet of paper to diffuse the beam. The purpose of the deflection arrangement (shown in Figure 2) was to continually monitor the laser output. A piece of paper was used to diffuse the beam to prevent the intense beam from falling directly onto the photomultiplier.



Block Diagram of Cloud Chamber Control System

E. Recording System

Piston position, chamber pressure, gas temperature and photomultiplier signal were simultaneously recorded on a Honeywell, Model 906C, multi-channel recorder. Thermocouples were connected to a thermocouple switch and null circuit then to a Keithley Model 155 null detector microvoltmeter which amplified the signal to feed the recorder. Using this method, room temperature was nulled out and only changes in temperature were recorded. Where exact temperatures were required, a potentiometer was employed and thermocouple potentials were recorded manually.

F. Photography

The cloud was photographed using a 35 mm single lens reflex camera. Photographs taken through the view port on top of the chamber were required for droplet density counts. Since extreme magnification was desired, a 75 mm lens with bellows was employed. With the lens and bellows arrangement a magnification of very nearly one was achieved at the film plane. All photographs were taken on Kodak Panatomic-X film. Due to high light level requirements for density photographs, a 100 joule xenon flash lamp was used. The flash lamp was mounted at the focal point of a cylindrical mirror to provide approximately parallel light. The flash tube was set approximately eighteen inches from the center of the chamber. Cloud photographs were taken from the side using the same camera with 50 mm and +3 copy lens.

G. Temperature Control

To control the temperature of the liquid in the chamber there was affixed to the stainless steel chamber base two coils of copper tubing through which circulated a methanol-water solution. The temperature of the solution was regulated by a constant temperature bath. Bath temperature was variable from -15° to $+70^{\circ}$ centigrade.

The chamber proper was covered with a plywood box to keep out stray light and facilitate temperature control of the immediate chamber environment. A variac controlled heating coil was placed inside the box. Air was circulated throughout the box by a small fan. To adjust the box temperature below room temperature, dry ice was added and the temperature controlled via the heating coil. Chamber atmosphere temperature could be easily controlled by changing the box temperature.

III. THEORY OF ANALYSIS OF CLOUD DENSITY DATA

In Langmuir and Schaefer's work in evaporation through monolayers it was proposed that the resistance to evaporation, which is proportional to the inverse of the evaporation rate, is the quantity to consider since monolayers offer a resistance to diffusion. They propose that evaporation resistance may be defined in analogy with Ohm's Law as

Resistance = Driving Force/Current. (1)

Adapting this idea to the cloud chamber, recognizing that differences in surface tension of a liquid relate to differences in resistance to diffusion through that surface, a method has been developed which permits variations in evaporation to be established from a measure of cloud density at equilibrium. The cloud density variations are related through this relationship to the surface tension of the water base under various environmental conditions. This is an entirely new approach to cloud chamber analysis. Although the uncertainty of the data collected and an approximation made for a constant occurring in the theory do not permit other than qualitative estimates of evaporation at present, the method of analysis is sufficiently unique that it is presented here in detail.

Consider a cloud chamber with a liquid base which is held in an expanded state until thermodynamic equilibrium is established and which is then compressed in preparation for an additional expansion. Immediately on compression, the vapor density throughout the chamber is lower than the equilibrium vapor density at that pressure and a given time, t, is required for equilibrium to be reestablished. If we let ρ = vapor density at the top of the chamber when expanded and ρ_0 = vapor density

just above the surface of the liquid, and also let ρ' = vapor density at the top of the chamber after compression and ρ'_0 = vapor density just above the surface of the liquid, we can state that ρ' = ρ initially and an unstable condition exists with ρ'_0 > ρ . As the diffusion process proceeds there is a net positive transport of water vapor through the liquid surface, resulting in a flow of vapor molecules upward, which we call a positive current. Following Langmuir, we then define a Driving Force which is proportional to the difference in vapor density between the bottom of the chamber and the top. That is,

Driving Force =
$$k'(\rho'\rho)$$
, (2)

where k' = constant of proportionality letting m = mass of water vapor in chamber volume V, A = liquid surface area (a constant), and t = time to establish equilibrium with vapor phase, we can define current as the mass of water vapor transported across the liquid surface of area A in the time t such that,

$$Current = \frac{m}{At}$$
 (3)

It is understood that vapor transport refers to the net transport across A, and when the liquid is in equilibrium with its vapor phase, the current is zero. Applying Equations (2) and (3) to Equation (1) we may write

$$R = k'(\rho_O' - \rho) \left(\frac{At}{m}\right), \tag{4}$$

where R = resistance to diffusion through a particular liquid surface and therefore the resistance to evaporation.

Let the subscript i denote an initial pure water state and the subscript f the altered state. The change (increase or decrease in resistance) is then given by

$$R = k' \frac{At}{m} [(\rho_{of}' - \rho_{f}) - (\rho_{oi}' \rho_{i})]$$

or
$$R = \frac{k}{m} [(\rho_{of}^{\dagger} - \rho_{f}) - (\rho_{oi}^{\dagger} - \rho_{i})]$$
 (5)

where k = k'At.

The mass of water vapor m is directly proportional to the cloud density, m α D, and since the vapor density is inversely proportional to the surface tension of the liquid, $\rho_O' - \rho \alpha \frac{1}{\gamma}$. Letting t equal the chamber "dead-time" (i.e., a constant) and employing the above proportionalities, we can write Equation (5) as

$$R = k \left[\frac{1}{\gamma_f D_f} - \frac{1}{\gamma_i D_i} \right]$$
 (6)

where k is a constant and R has units sec/cm.

It is easily seen that for

$$R \begin{cases} < 0, \frac{\gamma_{f}}{\gamma_{i}} > \left(\frac{D_{f}}{D_{i}}\right)^{-1} \\ = 0, \frac{\gamma_{f}}{\gamma_{i}} = \left(\frac{D_{f}}{D_{i}}\right)^{-1} \\ > 0, \frac{\gamma_{f}}{\gamma_{i}} < \left(\frac{D_{f}}{D_{i}}\right)^{-1} \end{cases}$$

$$(7).$$

and Figure 5 is a plot of this relationship with the R = 0 curve drawn in with k = 1 so that γ_f/γ_i = 1 and D_f/D_i = 1 for f = i. All points lying in the cross-hatched regions must be excluded from consideration since they do not correspond to real physical behavior.

The significance of Figure 5 becomes apparent when one considers a point in the R>0 region for γ_f/γ_i < 1. Any process which changes the liquid

surface (by addition of contaminants or other processes) such that a decrease in the surface tension occurs but at the same time increases the cloud density only enough to yield a point in the R>O region has exhibited a positive resistance to evaporation. If the cloud density increases beyond the value which pure water would have at that same surface tension ratio (i.e., crosses the R = 0 curve), the point would then fall in the R<O region and the process would have resulted in a negative resistance. For the evaporation resistance to be unaffected by a change in the surface tension, the point must fall on the R = O line. A corresponding analysis applies to the case where $\gamma_f/\gamma_i > 1$. Normalized to room temperature, the relationship for resistance takes a form expressed by

$$R = \frac{1}{\gamma_f D_f} -1 \tag{8}$$

Expressing the resistance in the form of Equation (8) enables one to plot R as a function of γ when appropriate.

With improvements in data collecting techniques associated with the cloud chamber and with calculated values of the constant k occurring in the resistance relationship, this method should ultimately lead to quantitative values of evaporation.

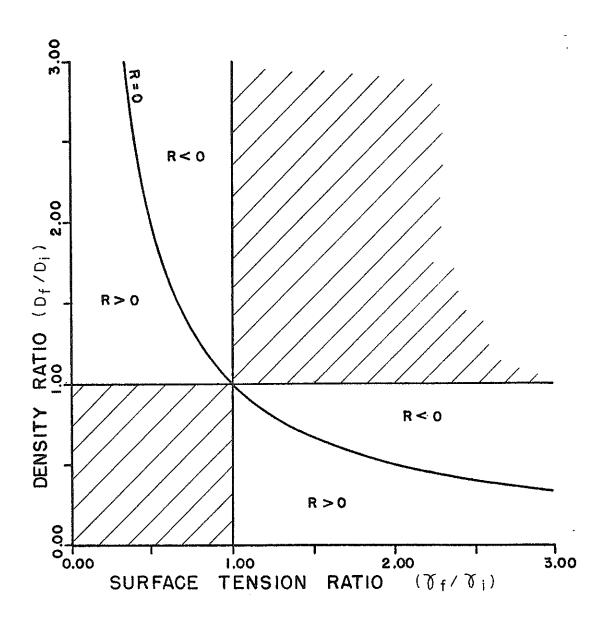


Figure 5
Graphical Interpretation of Equation 7, Data Analysis

IV. EXPERIMENTAL PROCEDURES AND RESULTS

The method developed in this project for the determination of evaporation from a body of water is new and all problems associated with the proper operation of the system have not yet been solved. The design continues to evolve during the collection of the data, and additions and modifications are continually being made as the special requirements of the evaporation study are understood.

Since cloud density is the measurement of primary interest in each of the experiments relating to evaporation, data was collected relating the drop density in a cloud to the photomultiplier signal recorded so that densities could be determined directly from the trace. Photography was used for this study and the drop density determined by a direct count. In spite of the excellent temperature, pressure, and displacement control and the use of methods of data collection already proven in previous experiments in this laboratory, large uncertainties exist in the value of the measured cloud densities. drop count method yields a very reliable density measure and is not responsible for the observed uncertainties; thus, it may be improper to assume that the cloud drop-size population is the same for every cloud formed under the varying conditions imposed on the chamber. Such an assumption was made in the analysis and on further examination may turn out to be in error. Also, the possibility that various combinations of chamber conditions might yield the same supersaturation and thus the same cloud density must not be overlooked. This has not yet been examined, but recent results from an attempt to reduce pure water, supersaturation-temperature data seem to imply that such is the case.

A. Calibration of the System

A discussion of the calibrations of the cloud chamber system is presented by Dodge¹⁴, a summation of which is offered here. In addition, certain operating procedures necessary to obtain reproducible conditions within the chamber were established and some of these are presented in this section also.

- 1. Chamber Volume. This calibration allows the expansion-ratio to be varied by altering the volume of water contained in the chamber. This is a very sensitive technique and is used throughout the experiment. An error of less than 0.25% exists in this calibration.
- 2. Pressure Transducer. The output of the pressure transducer was compared to a mercury manometer, a calibration procedure repeated at the beginning and end of each data run. An error of approximately 0.75% is associated with the output of the gauge.
- 3. Linear Transducer. Used for measuring expansion rates, the linear transducer was calibrated by recording the transducer trace at high recorder speed. At an expansion rate of 8.33 in/sec (the standard rate used in all of the experiments) which corresponds to an expansion time of 0.24 sec, the error in measuring the rate of expansion is about 4%. It is actually reproducible to within 1% since the expansion is mechanically controlled.
- 4. Photomultiplier. This calibration was performed by comparing the recorder galvanometer deflection with the laser beam intensity as measured by a Spectra Physics Power Meter. The signal error from the photomultiplier is negligible, the error in measurement of the signal trace from the recorder has been determined to be ±0.01 inches.

- 5. Thermocouple Calibration. Standard techniques were used here and temperature differences as small as 0.15°C could be observed. Temperatures measured were recorded on the same record with the pressure, linear transducer, and photomultiplier.
- 6. Clearing Field Voltage. Changing the clearing field voltage indicated that no effect on the cloud density occurred after the field reached a value greater than 50 volts. The field was set at 100 volts per cm of chamber depth for the remainder of the experiments since that is the value used by other investigators in drop growth experiments. Even large variations in this value are insignificant to the experiment.
- 7. Recorder Chart. Measurements could be made to ±0.01 inches and the ultimate error associated with the record depended on the magnitude of the signal recorded. Signals were attenuated or amplified by an Accudata 117, Multi-channel DC Amplifier so that the error resulting from the observation and measurement was minimized.
- 8. Time Delay. A time between expansion of 4 minutes ("dead-time") was established as the optimum time to yield the most reproducible cloud. For shorter times an oscillation of the cloud density was observed and longer periods produced no noticeable change from that of 4 minutes. This apparently is the time for this particular chamber to come to complete thermodynamic equilibrium and for reevaporation nuclei to fall out of the chamber.
- 9. Miscellaneous Items. In addition to the above, such things had to be established as the proper location of the photomultiplier, proper beam diameter for the laser beam, filters for continuous calibration of

the beam, calibration of the exhaust valve, proper camera exposures, etc. These determinations, and others, are all described in the Dodge reference.

B. The Evaporation Experiments

Six major experiments have been initiated and are at various stages of completion and interpretation. In addition, several supporting experiments were performed to supply information concerning such things as surface tensions, monolayer distribution methods, surface barrier thickness and heat transfer from the surface of a liquid. These are discussed by Loftin and are not reported on here. The data for all except the Surface Barrier Effect experiment are presented in Appendix A.

1. Atmospheric Structure Effect. Homogeneous nucleation rate investigations have shown the existence of a dependence on the nature of the gas present in the chamber atmosphere. For non-condensable gases, a result is obtained which cannot be predicted by classical nucleation theories 16. Since air contains non-condensable gases as well as others which are condensable, an experiment designed to observe the effect of changing the atmosphere in the formation of a cloud above a pure water surface was initiated. The result probably does not relate strongly to the evaporation process across the surface of the liquid, but does yield information about the dependence of the cloud formed on the composition of the chamber atmosphere.

Four gases were used in this experiment, three inert gases (nitrogen, helium, and argon) and air. The results shown in Figure 6 indicate clearly that a dependence does exist on the chamber atmosphere. This is reasonable

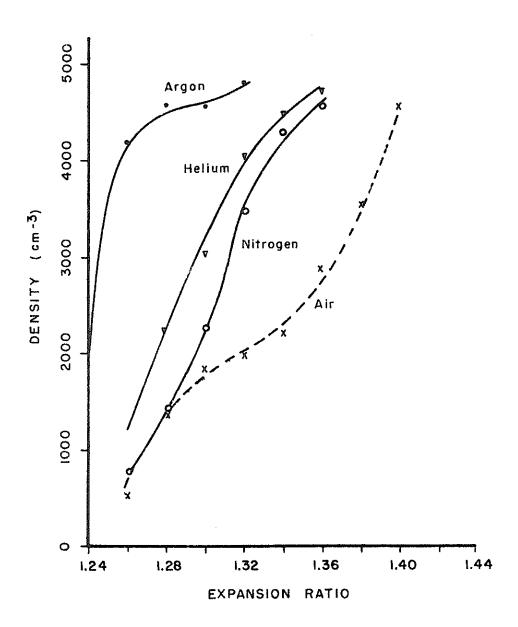


Figure 6
Cloud Density for Various Inert Atmospheres

in that a change in nucleation rate should yield a different drop size distribution within the cloud; however, since the assumption was made in the calibration of the photomultiplier that all clouds had the same drop-size distribution it is not clear how one should interpret the results. Other than for the general behavior, the results differ both in droplet densities and supersaturations from the data obtained in nucleation rate studies.

2. Temperature Gradient Effect. A vertical temperature gradient was established in the chamber by heating the chamber atmosphere. Since heating the atmosphere also tended to heat the water, the water was cooled by a methanol-water solution circulating about the chamber base. Water temperature was held as closely as possible to normal operating temperature (24.7°C). To measure the vertical temperature gradient, one thermocouple measured the temperature of the water surface while another measured the chamber atmosphere 10 cm above the water surface. As the temperature gradient was increased, the cloud density, as reflected in the output of the photomultiplier, appeared to decrease and could be reduced to almost zero at high temperature gradients.

To determine the structure of the cloud within the chamber photographs were taken from the side of the chamber. Illumination was provided by a xenon flash lamp, and photographs were taken at peak cloud density for temperature gradients from 0.05° C/cm to 0.9° C/cm, the gradient increasing upward in the chamber. To determine the cloud structure, a Jarrell-Ash Microphotometer (Model 23-050) was used to scan the 35 mm film negatives through the center of the chamber, and the result of these scans for the

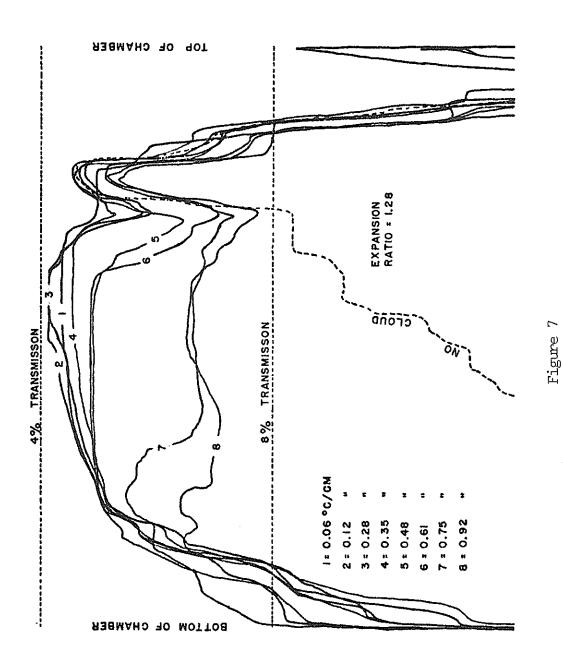
various temperature gradients is shown in Figure 7. An atmosphere of cleansed air and an expansion ratio of 1.28 was used for this experiment.

The results of this experiment indicate that the distribution of the droplets making up the cloud are indeed dependent on the temperature gradient above the surface of the liquid and that when gradients of the order of 1°C/cm exist, the cloud develops very close to the liquid surface. This is consistent with development of fog close to the cool earth surface in the early morning. Of interest for future experimental work, however, is the fact that until a gradient of about 0.6°C/cm occurs, the cloud development is very uniform throughout the chamber. This result is important in any cloud study and of special interest if large cloud chambers are employed or if various chamber temperatures are used in an experiment. As a result of this experiment, the temperature gradient in the remaining experiments was maintained at very small values - usually less than 0.1°C/cm.

3. Surface Tension Effects. The technique developed for data interpretation, discussed in Sec III and displayed in Figure 5, predicts the results one should obtain if the surface tension of pure water is varied from its value of 72.01 dynes/cm at the temperature of 24.7° C chosen as the standard for this study. The R = 0 curve, no change in resistance from that of pure water, represents the variation in cloud density as a function of changes in the surface tension.

Experiments were performed in which the surface tension of pure water was altered by controlling the temperature of the cloud chamber.

Temperatures ranging from 12°C to 35°C were established and cloud densities



Microphotometer Scan of Clouds for Various Temperature Gradients

obtained as a function of temperature. Many problems were encountered during the course of this experiment; however, data were obtained at approximately 1°C intervals and the results analyzed according to the method of Sec III. The data points are displayed in Figure 8. As the surface tension decreases (with increasing temperature), it is evident that the data representing cloud density fall in the R<0 region, indicating a decreasing resistance to evaporation. Similarly, increasing surface tension results in points falling in the increasing resistance region, R>0.

In analyzing these data, it became clear that effects due to supersaturation changes associated with the chamber temperature alteration must be removed from the raw data before it can be used to establish the actual R = 0 curve. A program established to carry out these reductions has been unsuccessful to date due to pressure errors which occurred during the collection of the data which were unobserved until the reduction program was initiated. Also, the character of the cloud at low temperatures is in doubt. At the lower temperatures, the chamber atmosphere reaches a temperature below 0°C after expansion and it is very probable that ice crystals have developed in the cloud. If this is so, the scattered signal would be substantially different than that from a cloud composed of a collection of water droplets. This would lead to a misinterpretation of the photoelectric signals. Even with these effects masking the true value of the cloud density for a given surface tension, the behavior of the data is such as to support the validity of the interpretation of Sec III. In order to illustrate the scatter among the data in this experiment, Figure 9 presents the data plotted according to

Equation (8) which relates R and γ.

4. Monolayer Effect. Investigators have reported that certain long-chain alcohols, when distributed as monolayers on the surface of a liquid, act as inhibitors to evaporation from that liquid $^{\rm l}$. Among those monolayers most investigated and used in experimental application are the following: Dodecanol ($\rm C_{12}H_{25}OH$), Tetradecanol ($\rm C_{14}H_{29}OH$), Hexadecanol ($\rm C_{16}H_{33}OH$), and Octadecanol ($\rm C_{18}H_{37}OH$). Of these alcohols, the best inhibitor is considered to be Octadecanol. Evaporation resistance as a function of surface pressure, a quantity described in detail in La Mer 17 , shows that as the number of carbon atoms increase, the resistance to evaporation increases. For our monolayers we should then find that Dodecanol has the least effect on evaporation and Octadecanol the greatest effect.

The application of the chamber to the study of monolayers proved to be a very difficult experiment and the results are inconclusive except in a qualitative sense. The data do indicate that Dodecanol is an inhibitor to evaporation and apparently the poorest of those tested. The data are plotted on Figure 8 and it can be seen that the points fall in that region corresponding to an increase in resistance to evaporation, R>0. It was expected that some relationship would be observed between the various alcohols and the resistance. However, the only conclusive result is that the resistance of the Dodecanol is less than that of the others. (That is, the others lie farther from the R = 0 curve than Dodecanol.) To try to detect any relationship which might exist and be hidden by the fact that the alcohols lie at different points on the

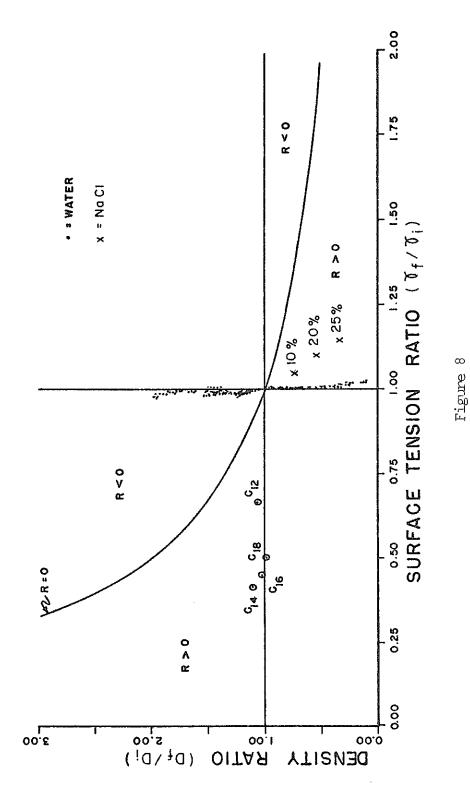
surface tension axis, the resistance relationship given by Equation (8) has been plotted and is shown in Figure 10. The difference in resistance between the Dodecanol and the other alcohols is clear. Less clear is any relationship between the remaining alcohols, especially one corresponding to that reported in the references.

Many uncertainties were involved in the collection of these data, and in light of that fact, the results are reasonably good. It was necessary to determine the surface tension of each of the alcohols when covering the liquid, clear the chamber of unwanted vapors (the ether solvent used for all the alcohols except Dodecanol), lay down a monolayer which completely covered the liquid surface, and determine the cloud density. The total uncertainties associated with these measurements and processes could be quite large.

5. Dissolved Contaminant Effect. The cloud chamber study of evaporation seems to be a very promising method for the study of the effect of dissolved or suspended substances on the evaporation of water. When a salt, for example, is dissolved in water, the effect is to alter the surface tension of the water and thus alter the resistance to evaporation of molecules through the surface. Unitl the percentage contaminant is very high, the dominant molecule in the liquid is still the water molecule and the result of changing the surface tension should be basically one of altering the evaporation rate of water. The initial results of an experiment in which sodium chloride was dissolved in pure water support the claim that the cloud chamber technique can be used to yield good qualitative and quantitative results.

Sodium chloride was dissolved in water until a 10% by weight solution was obtained and the cloud density observed. The solution was then changed to a 20% concentration of sodium chloride, and later to a 25% concentration and the cloud density measurements made for each case. The results are shown plotted on Figure 8 and also on Figure 11, and a very obvious relationship exists between the concentration of the salt in the water and the resistance to evaporation. The 10% solution produced a decrease of approximately 15% in the cloud density with the 20% and 25% concentrations producing decreases of approximately 43% and 67% respectively. These changes are much larger (especially at the higher concentrations) than changes in evaporation reported by Turk due to salts in solution. However, the behavior is qualitatively the same and definitely establishes the fact that a solution of salt water evaporates more slowly than fresh water.

Several differences exist between this experiment and that of
Turk which could well account for the large differences in evaporation
reduction observed in the two experiments. His experiment was performed
in the field (Bonneville Salt Flats) under varying meteorological conditions while ours was under controlled temperature and pressure conditions.
His solution contained large quantities of other salts in addition to
sodium chloride while ours was a mixture of granular, laboratory grade
sodium chloride and doubly distilled water. His method of determining
evaporation was a standard method used for many years while ours was a
newly devised technique where the results are obtained from a measure of
cloud density. It is by no means certain that an observed percentage



Graphical Interpretation of Equation 7, Experimental Data

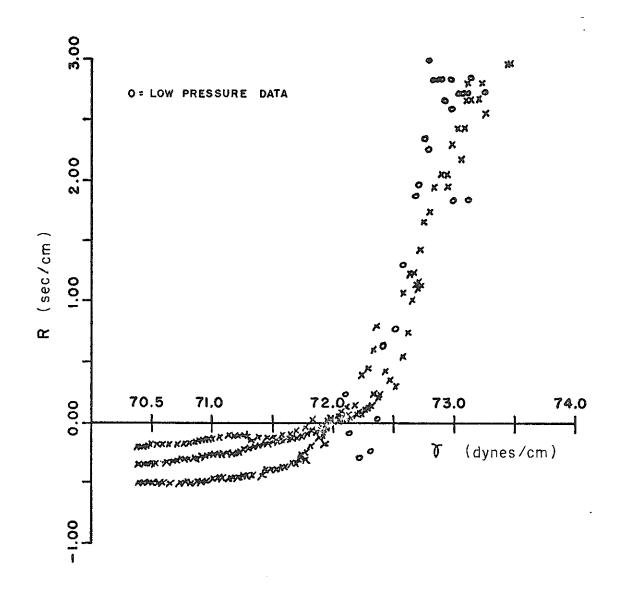
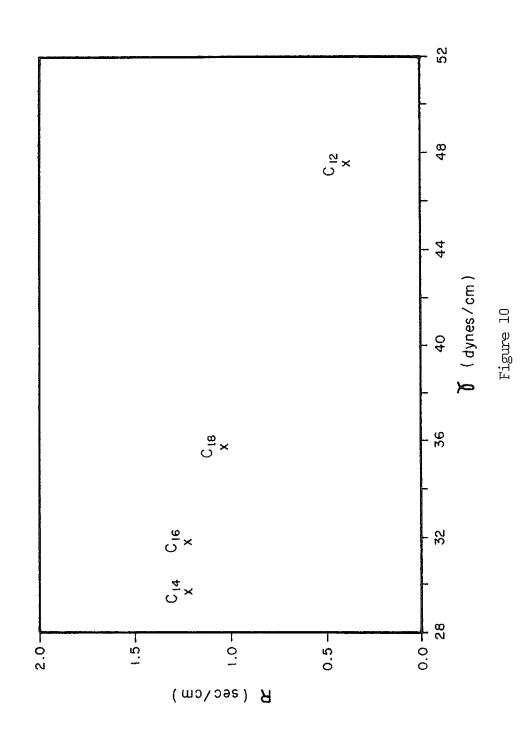
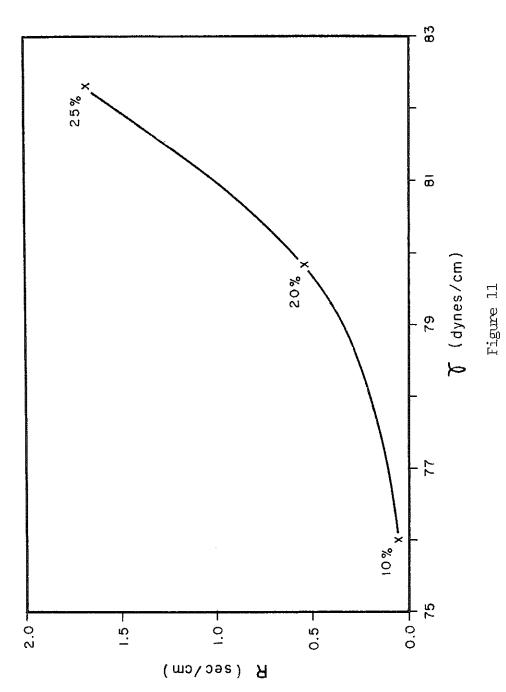


Figure 9

Evaporation Resistance versus Surface Tension for Water



Evaporation Resistance versus Surface Tension for Various Alcohol Monolayers



Evaporation Resistance versus Surface Tension for Various Concentrations of Sodium Chloride

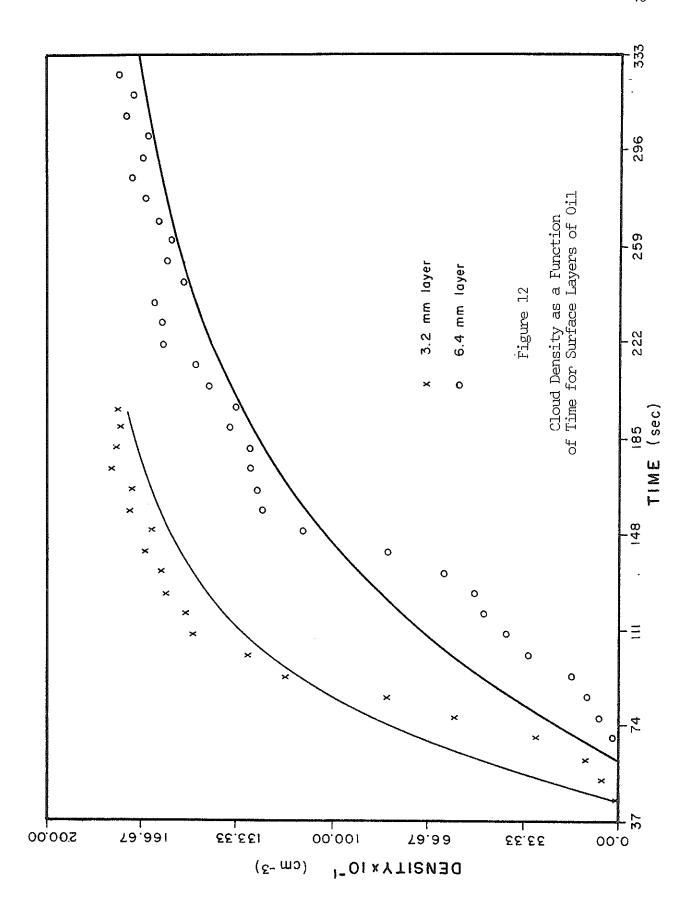
difference in cloud density relates directly to differences in evaporation. In fact, the relationship expressed by Equation (8) indicates that this is, in fact, not the case.

Calcium chloride and methanol were also investigated in the same manner as that described above, each of them yielding an increase in evaporation rather than a reduction. These two substances yielded results which are not as definitive as that of sodium chloride as far as evaporation is concerned, but are valuable results otherwise. As a result of the experiments with calcium chloride, it is clear that difficulties arise if substances which undergo an exothermic reaction with water are used in the chamber. Then thermodynamic equilibrium is difficult to establish, and the cloud density determinations are highly uncertain. The methanol experiment again demonstrated the difficulty of using the chamber for the examination of substances with a low vapor pressure. It is difficult to keep the chamber atmosphere free of the methanol molecules and the resulting clouds are very dense. Analysis of these data are not presented in this report.

6. Surface Barrier Effect. This effect was examined by spreading uniformly over the surface of the liquid a known thickness of Welch Duo-Seal Vacuum Pump Oil. The purpose of the experiment was to establish procedures for observing the growth in density of a cloud as a function of time and to examine the procedure for obtaining the evaporation rate from such observations. Normally, in the other experiments already described, cloud development takes place so quickly that the chamber has not had time to reach thermodynamic equilibrium before the cloud is fully developed.

It is not possible, then, to get direct measurements of rate of evaporation except for such effective barriers as oil or other covers through which water vapor molecules diffuse very slowly.

The results of this experiment with two thicknesses of oil are shown in Figure 12, and it is seen that rates of evaporation can readily be obtained in such an experiment. The process accounting for the variations in the cloud growth rate is not yet clear, but apparently water molecules which diffuse through the barrier and then condense out into droplets return to the top surface of the oil and are available for the next expansion. Then these molecules, in addition to those that pass through the barrier during the next "dead-time" period, form a slightly more dense cloud, until finally a water table exists above the entire layer of oil and a cloud of the density expected for water at the given surface tension is formed. The rate of evaporation is obtained by taking the slope of the curve formed by the cloud data points. It can be seen that the evaporation rates change with time as well as with thickness of the barrier.



V. CONCLUSIONS

The objectives stated in this report have been completed to the approximate degree predicted in the original proposal.

Objective (1). The design and construction of a cloud chamber and associated equipment for use in evaporation studies has been completed. This does not mean that further changes may not be necessitated as new requirements are established, but that the initial goal has been met for the design of a chamber of sufficient versatility and control of operation, and for the establishment of precision techniques of cloud density determination, to enable the system to be used in the study of water evaporation. It has been shown that for certain applications (e.g., the study of the effect of surface barriers, dissolved or suspended contaminants, atmospheric structure), the cloud chamber method is presently capable of producing qualitative and relative measures of evaporation. For investigations involving temperature changes, monolayer covers, and low vapor pressure materials, further refinement of technique is required.

Objective (2). The investigation of evaporation as a function of various parameters has been initiated and at least six major experiments performed. These experiments yielded valuable information concerning the possible future application of this approach to the study of evaporation and at least one, Experiment 5, demonstrated a technique for the study of dissolved contaminants which could be of great importance. For example, a detailed study of various salts in controlled concentrations, alone or in combination with other substances, can be made and an analysis of the

resulting evaporation retardation or enhancement related to the molecular structure of the substance, its concentration, and its effect on the properties of the liquid. Experiment 6 has shown that the cloud chamber method can be used to examine the effect of surface barriers (not monolayers) on the evaporation of the liquid and that one can obtain evaporation rates directly from the data. The experiment can be performed in a short time (the order of hours rather than days or weeks as for evaporation pan experiments) and the evaporation rate as a function of thickness can be determined with ease. The rates are not reported here for the two thicknesses of oil examined in this experiment since they are presented at this time only to serve as an example of the capability of the system. Experiment 5 and Experiment 6 will be repeated in detail and many substances examined. The results of this work will constitute the material for a future publication.

Objective (3). A quantitative relationship between evaporation rate and certain important parameters has not yet been established. It was pointed out in the original proposal that this would not be attained during the three years requested for support of the work but that it is the ultimate goal of the study. An analytical method of analysis has been developed which, at present, yields qualitative evaluations of the effect of various parameters on evaporation and which should eventually lead to quantitative measures of evaporation. The analysis must rely, of course, on the precision of the measurement available. This is marginal in some instances and must be improved before a satisfactory analysis can be attempted. The possibility of relating the evaporation process

directly to the surface tension, and ultimately, to the diffusion through the surface of the liquid has been demonstrated.

The project has revealed the value of a chamber system which can be brought to thermodynamic equilibrium very quickly (\sim 1 sec) and the possibility of designing such a could chamber is now being examined.

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APPENDIX A

TABULATION OF DATA

ASSOCIATED WITH THE EXPERIMENTS

The tabulation of data presented in Appendix A represents the data collected for Experiments 1 through 5. Experiment 6 is not presented since it is simply a two-column listing of cloud density as a function of time, and every point is plotted on Figure 12.

The value of each data point on the listing is a representative value obtained from at least five separate repetitions of the experiment. The uncertainties are not listed with the data but are estimated in Part IV, Sec. A.

DEFINITIONS OF TABLE HEADINGS

No. = Data Point Number

T = Temperature of Water Surface in Degrees Centigrade

H = Photomultiplier Trace Deflection in Inches

D = Cloud Density in Droplets per Cubic Centimeter

G = Surface Tension (gamma) in Dynes/Cm

Resist. = Evaporation Resistance in Sec/Cm

F and I Denote Final and Reference States Respectively

DEFINITIONS OF TABLE HEADINGS.

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1 = TEMBERATURE DE NATER SUBEACE IN INCHES.

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3 = SUBFACE TENSION (GAMMA) IN OYNIS/CM.

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, i.i.	<u>1</u> 1	<u>-</u>	발 고	ī	HF/HI	논	10	DF/01	GF.	19	GF / G1	49, TE TI HE 41 HE/HI OF DI DE/DI GF GI GE/GI RESIST.
CALCIUM C	1.1L03	1DE (1	ر ارو									
24.	7.0	24.70	0.92	0.74	24,70 24,70 0,92 0,74 1,1032 1498,0 1326,0 1,1297 66,56 72,01 0,9243 -0,042	1498.0	1326.0	1.1297	66.56	72.01	0.9243	-0.042
SALCTUM CHLORIDE (20%)	THOR	1DE (2	120									
54.	0,	24,70	0.19	0.74	24.70 24.70 0.79 0.74 1.0576 1456.0 1326.0 1.0981 64.01 72.01 0.8889 0.025	1456.0	1326.0	1.0981	64.01	72.01	0.8889	0.025
CALCIUM CHLORIDE (252)	HUR	105 (2	57.1									
24,70 24,70 0.91 0.74 1.2297 1521.0 1326.0 1.2225 61.01 72.01 0.8472 -0.035	6,	24.70	0.91	0.74	1.2297	1521.0	1326.0	1.2225	61.01	72.01	0.8472	-0.035
CALCIUM CHLOYIDF (30%)	.HL0₹	10F (3	(20)									
54.	. 70	24.70	0.86	0.74	1.1621	1554.0	1326.0	1.1719	52.06	72.01	0.7230	0.18)
COPK DUST	0	1 GRAM	is)									
24.73 24.76 0.75 0.74 1.0135 1350.0 1326.0 1.0181	73	24.70	0.75	0.74	1.0135	1350.0	1326.0	1.0191		1		1 1 1 1 1
YETHANJL	C 0%	-										
24.	5.	24.70	4.20	0.74	5.6753	2320.0	1326.0	2,1268	58.15	72.01	0.4076	-0.419
4ETHANDL (20%)	1203	=						•				
24.	CZ,	24.70	4.39	0.74	5.7312	2886.0	1326.0	2-1763	46 6 6	72.01	0.6935	-0.337
4ETHANJL (5.0%)	(5.0%	=										
24,	70	24.70	6.30	0.74	24.70 24.70 6.30 0.74 8.5106 1326.0 34.92 72.01 0.4849	1	1326.0	1 1 1 1 1 1	34.92	72.01	0.4849	