A STUDY OF CONDENSATION
AND THE
OPERATION OF DIFFUSION CLOUD CHAMBERS

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CONTENTS

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PREFACE

This thesis is an account of some investigations into the process of condensation and the operation of cloud chambers, with special reference to diffusion chambers.

In the beginning of 1951, verbal reports from the United States of the revived interest in continuous diffusion chambers suggested an investigation into the design and operation of these chambers. When this investigation was started, Langsdorf's (1939) paper was the only publication on the subject, but soon the papers of Cowan (1950) and Needels & Nielsen (1950) became available. The diffusion chamber then constructed here incorporated some improvements in the design, and the paper describing it was the first account given of a chamber operated outside the United States. With this chamber many features of diffusion chambers were noted independently of other workers. In particular, the effect which an electric field has on the operation of the chamber seems to have been clearly understood here.

It was originally hoped that it would be possible to use a diffusion chamber as well as an expansion chamber for experiments on condensation; however, it became clear eventually that the diffusion chamber could not be used for such experiments owing to the difficulty of measuring the conditions (temperature, vapour concentration) inside the chamber. On the other hand, the understanding of the operation of the chamber requires some knowledge of the process of condensation. The description of the work on diffusion chambers thus fits in logically at the end of the thesis, constituting Part IV.

In Part I the theory of condensation is discussed. The existing theories on the subject are critically reviewed, and the relation between them clearly indicated. Much of the interpretation is original, and in particular, a thorough investigation of the calculations showed clearly that, contrary to the previous conceptions, the condensation does depend critically on the properties of small complexes of vapour molecules.

Some experiments with expansion chambers on the condensation of supersaturated vapours are described in Part II. The observed variation in drop density with expansion ratio is compared with the theoretical predictions in Part I, with due consideration to the experimental conditions.

The experimental work on condensation was extended to a study of the condensation nuclei produced by ultra-violet light; this work is described in Part III. Various properties of these nuclei were discovered, such as the ability of single nuclei to promote condensation. The experiments also indicated conclusively the origin of the nuclei, and explained some of the conflicting results obtained in previous investigations on the subject.

The author has worked independently upon the parts of the thesis which describe new experimental and theoretical advances. Where any specific information and assistance has been given by other persons, it has been clearly indicated. In general, however, I have had many useful discussions with Professor P. I. Dee, Mr. J.R. Atkinson and Dr. G.A.P. Wyllie. It is a pleasure to thank the above for their sustained interest in the research.

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PART I

THE THEORY OF CONDENSATION OF SUPERSATURATED VAPOURS

INTRODUCTION

It has been known for a long time that when a gas saturated with water vapour is expanded, the vapour becomes supersaturated and will then condense on any available nuclei in the form of dust particles. The necessity for the presence of these nuclei was understood from the theory given by Kelvin (1870), who showed that the equilibrium vapour pressure over a convex surface is increased by surface tension.

The early experiments were done with rather slow expansions, so that the maximum supersaturations reached were relatively small. In a series of classical experiments C.T.R. Wilson (1897, 1899) showed that condensation will nevertheless take place in a clean damp gas if a sufficiently large adiabatic expansion was made. At about fourfold supersaturation, a rainlike condensation was observed to set in, and this Wilson ascribed to condensation on ions present in the gas. At about eightfold supersaturation, Wilson started to observe a dense cloud. He suggested that the dense condensation took place on aggregates of vapour molecules, independent of the presence of other substances. This explanation has been confirmed by later workers.

The condensation on ions had been understood from the early theory of J.J. Thomson (1888), who had extended Kelvin's theory to charged drops. The condensation on aggregates of vapour molecules presented a more difficult problem, and it was much later before a quantitative theory was developed by Volmer & Weber (1926) and Farkas (1927). The thermodynamic arguments of these workers were extended by Becker & Döring (1935) and Frenkel (1946), who discussed the actual kinetics of the condensation process. Becker & Döring obtained an expression for the rate of drop formation which seems to be in good agreement with the measurements of Volmer & Flood (1934). The present investigation shows, however, that the Becker & Döring and Frenkel treatments are open to criticism, and that they should be regarded as only first approximations to the theory of condensation.

CONDENSATION IN THE ABSENCE OF IONS

Consider a supersaturated vapour, such as exists in a cloud chamber after a fast expansion. If the vapour can be treated as a perfect gas, then, as shown by Kelvin (1870), a drop of radius r^* will be in equilibrium with the vapour if

$$\ln \frac{p}{p_\infty} = \frac{2M\sigma}{dRT}\,\frac{1}{r^*} \,. \qquad (1)$$

Here M is the molecular weight of the liquid, R the gas constant, d the density and σ the surface tension of the liquid, T the absolute temperature of the vapour and the drop, p the actual vapour pressure and p_∞ the equilibrium vapour pressure over a plane surface of the liquid at temperature T. The ratio p/p_∞ is usually referred to as the supersaturation S.

The equilibrium between the drop of radius r^*

and the vapour is unstable, as can be seen from Equation (1): larger drops are supersaturated with respect to the vapour and tend to grow, while smaller drops are undersaturated and tend to evaporate. Thus Kelvin's theory does not suggest a mechanism whereby a drop of radius r^* may be grown from small molecular complexes. These complexes are formed in a vapour when the molecules stick together for some time after gas-kinetic collisions. The size of the complexes may fluctuate considerably, however, as the result of the condensation and evaporation of single molecules. There is thus always a finite probability that some of the complexes may grow to a size beyond the critical radius r^* and from there to visible drops. This probability is indeed negligible if the vapour is just supersaturated, but it is found that the probability of drop formation increases rapidly with increase in the supersaturation. At sufficiently high supersaturations, drops will therefore be formed in observable quantities. The transition from the condition where virtually no drops are formed to where drops can be observed, is quite sharp, and one can therefore speak of a critical supersaturation at which it occurs.

The theory concerns itself mainly with condensation at supersaturations near the critical value. Under these conditions, the total number of molecules in complexes is negligible compared to the number of single molecules. The vapour pressure is therefore in practice due to the single molecules only, and may be considered constant during the initial condensation process. It is furthermore assumed that the permanent gas serves to equalize the temperature of the vapour and the small droplets.

The Becker & Döring Calculation

Bearing these considerations in mind, Becker & Döring therefore simplified the problem by considering the following idealised condition. A supersaturated vapour, vapour pressure p, is enclosed in a large container. Drops may form and grow, and they are removed as soon as they reach a certain size, the vapour pressure being maintained constant by the continuous introduction of single molecules. There will thus be a steady flow of molecules from one drop size to the next.

Let r_g be the radius and s_g the surface area of a drop consisting of g molecules; r^* the radius of a drop of g^* molecules, the drop being in equilibrium with the vapour; n_g the number of drops per cm^3, consisting of g molecules; α_g the probability per second per cm^2 of surface area, that a molecule will evaporate from a drop of g molecules; β_g the probability per second per cm^2 of surface area, that a molecule will condense on a drop of g molecules; and I the number of drops, consisting of G molecules ($G \gg g^*$) removed per cm^3 per second.

Then for all values of g less than G,

$$I = \beta_{g-1} s_{g-1} n_{g-1} - \alpha_g s_g n_g \quad , \tag{2}$$

$$= \beta_{g-1} S_{g-1} - \alpha_g S_g \quad , \tag{3}$$

where $S_g = s_g n_g$. Writing (3) in full,

$$I = \beta_1 S_1 - \alpha_2 S_2 \quad ;$$

$$I = \beta_2 S_2 - \alpha_3 S_3 \quad ;$$

$$. \quad . \quad . \quad . \quad . \quad .$$

$$I = \beta_{G-1} S_{G-1} \quad ;$$

since $S_G = 0$. To eliminate the unknown S_g's from these equations, the second is multiplied by α_2/β_2, the third by $\alpha_2\alpha_3/\beta_2\beta_3$, etc., and the resulting equations added, giving,

$$\frac{\beta_1 S_1}{I} = 1 + \frac{\alpha_2}{\beta_2} + \frac{\alpha_2\alpha_3}{\beta_2\beta_3} \quad . \; . \; . \quad \frac{\alpha_2\alpha_3\cdots\alpha_{G-1}}{\beta_2\beta_3\cdots\beta_{G-1}} \; . \qquad (4)$$

For large values of g, and assuming the condensation coefficient to be unity, β_g will tend to the constant value β given by kinetic theory

$$\beta = p(2\pi mkT)^{-\frac{1}{2}} \quad . \qquad (5)$$

Assuming that α_g is proportional to the equilibrium vapour pressure over a drop of g molecules, (this is not strictly correct as is shown in the next section) we have for the equilibrium drop

$$\alpha_{g^*} = \beta \qquad ,$$

and therefore for large drops

$$\frac{\alpha_g}{\beta_g} = \frac{\alpha_g}{\alpha_{g^*}} = \frac{p_g}{p} = \mathrm{Exp}\left\{\frac{2M\sigma}{dRT}\left(\frac{1}{r_g} - \frac{1}{r^*}\right)\right\}$$

$$= \mathrm{Exp}\left\{\frac{2M\sigma}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3}\left(g^{-1/3} - g^{*-1/3}\right)\right\}, \qquad (6)$$

where p_g is the equilibrium vapour pressure over a drop of radius r_g, and m is the mass of a vapour molecule. Assuming for the moment that this formula holds down to g = 2, this gives

$$\frac{\alpha_2\alpha_3\cdot\cdot\alpha_g}{\beta_2\beta_3\cdot\cdot\beta_g} = \mathrm{Exp}\left\{\frac{2\sigma M}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3}\left(\sum_{\nu=2}^{g}\nu^{-1/3} - (g-1)g^{*-1/3}\right)\right\} \qquad (7)$$

As will be seen later, the important values of g are those near the critical value g^*, which is quite large (e.g. in the case of water vapour, under conditions normally occurring in cloud chambers, about 70), so that the sum occurring may be replaced by the integral

$$\int_1^g g^{-1/3}\,dg = 3(g^{2/3} - 1)/2 ,$$

giving

$$\frac{\alpha_2\alpha_3\cdot\cdot\alpha_g}{\beta_2\beta_3\cdot\cdot\beta_g} = \mathrm{Exp}\left\{X\left[3\left(\frac{g}{g^*}\right)^{2/3} - 2\left(\frac{g}{g^*}\right) - 3g^{*-2/3} + 2g^{*-1}\right]\right\} \tag{8}$$

where

$$X = \frac{\sigma M}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3} g^{*2/3} . \tag{9}$$

Hence

$$\frac{\beta_1 s_1}{I} = \mathrm{Exp}\left\{-X(3g^{*-2/3} - 2g^{*-1})\right\}\sum_{g=2}^{G-1}\mathrm{Exp}\left\{X\left[3(g/g^*)^{2/3} - 2(g/g^*)\right]\right\} \tag{10}$$

In this expression the sum is again replaced by an integral,

$$\int_1^{G-1}\mathrm{Exp}\left\{X\left[3(g/g^*)^{2/3} - 2(g/g^*)\right]\right\}dg . \tag{11}$$

Now as X is quite large (e.g. in the case of water vapour, about 50), the integrand has a very sharp maximum value e^X at $g = g^*$, decreasing rapidly to zero on both sides. A very good approximation to the integral may therefore be obtained by substituting

$$y = (g/g^*)^{1/3} - 1 , \qquad (12)$$

so that in the range where the integrand is significant, y may be neglected compared to unity. Furthermore, the limits may be extended to $+\infty$ and $-\infty$, so that the integral becomes approximately

$$\begin{aligned} & 3g^* e^X \int_{-\infty}^{+\infty} (1 + y)^2 \mathrm{Exp}(-3Xy^2 - 2Xy^3)\,dy \\ = \ & 3g^* e^X \int_{-\infty}^{+\infty} \mathrm{Exp}(-3Xy^2)\,dy \\ = \ & 3g^* e^X (\pi/3X)^{\frac{1}{2}} \ . \end{aligned}$$

This gives

$$I = \frac{\beta_1 S_1}{g^*}\sqrt{\frac{X}{3\pi}}\ \mathrm{Exp}\left\{-X(1 - 3g^{*-2/3} + 2g^{*-1})\right\} \qquad (13)$$

$$= \frac{\beta_1 S_1}{g^*}(X/3\pi)^{\frac{1}{2}}\ e^{-X} \ , \qquad (14)$$

if $3g^{*-2/3}$ and $2g^{*-1}$ are neglected compared with unity.

The last approximation is not really justified in liquids normally used in cloud chambers. For example, in the case of water vapour at 261°K at a supersaturation of 5.05, $g^* = 70$, so that $3g^{*-2/3} = 0.17$. The effect of retaining the term $3g^{*2/3}$ is examined later.

In any case, it is clear that Kelvin's formula does not necessarily apply to very small drops. Becker & Döring justify their assumption that α_g/β_g is given by (6) even for small values of g, by stating that the sum

$$1 + \frac{\alpha_2}{\beta_2} + \frac{\alpha_2\alpha_3}{\beta_2\beta_3} + \ldots \qquad (15)$$

is affected only to a small extent by the values of α_g/β_g for small g. This is not correct, because even though the initial terms in (15) are indeed negligible, the product of α_2/β_2, α_3/β_3, etc., occur in the term

$$\frac{\alpha_2\alpha_3 \ldots \alpha_{g^*}}{\beta_2\beta_3 \ldots \beta_{g^*}} \quad . \qquad (16)$$

It may be seen, for instance from the approximate Equation (8), that this is the maximum term in the sum (15). Since the sum is of the same order of magnitude as this maximum term, it does therefore depend markedly on the values of α_2/β_2, α_3/β_3, etc. At this stage the actual values of these fractions are unknown, but even if they differ only slightly from (6), their product may still cause the critical term (16) to deviate significantly from the value given by (8). Hence the expressions (13) and (14) for the condensation rate I, must be regarded as first approximations only, until fuller knowledge of the properties of small complexes becomes available.

The Frenkel Treatment

Frenkel (1946) has given an alternative mathematical treatment, which has recently been reviewed by Farley (1952). Frenkel eliminates the α_g's in (2) by means of a function N_g which is defined by the equation

$$N_g s_g \alpha_g = N_{g-1} s_{g-1} \beta_{g-1} \quad , \tag{17}$$

where $N_1 = n_1$. Using this function, (2) can be written in the form

$$I = N_{g-1} s_{g-1} \beta_{g-1} \left(\frac{n_{g-1}}{N_{g-1}} - \frac{n_g}{N_g} \right) \quad . \tag{18}$$

For large values of g this may be written approximately as

$$I = -N_g s_g \beta_g \frac{d}{dg} \left(\frac{n_g}{N_g} \right) \quad . \tag{19}$$

Hence

$$1 = \frac{n_1}{N_1} = I \int_1^{\sigma} \frac{dg}{\beta_g s_g N_g} \quad . \tag{20}$$

To find an expression for N_g, it will be seen from (17) that in the case when the vapour is undersaturated or just saturated, N_g represents the equilibrium distribution of drops consisting of g molecules. When the vapour is supersaturated, such a physical interpretation is no longer possible, since the total number of drops N_g is then found to diverge. Equation (17) shows, however, that N_g is only a function of the α's and β's, so that for the supersaturated vapour it will still be given by the same analytical expression as for the equilibrium state. This expression is shown by Frenkel from thermodynamical considerations to be

$$N_g = N_1 \exp\left\{X\left[2(g/g^*) - 3(g/g^*)^{2/3}\right]\right\}. \qquad (21)$$

Substituting this expression for N_g into (20) gives

$$1 = \frac{I}{N_1}\int_1^G \frac{\mathrm{Exp}\left\{X\left[2(g/g^*) - 3(g/g^*)^{2/3}\right]\right\} dg}{s_g \beta_g} \qquad (22)$$

Since the value of X for liquids used in cloud chambers is quite large, it follows that $1/N_g$ has a strong maximum at $g = g^*$. The terms $s_g\beta_g$ may therefore be taken outside the integral and the limits extended from 0 to ∞. On putting β_{g^*} equal to β, this gives

$$\frac{\beta s_{g^*} N_1}{I} = \int_0^\infty \mathrm{Exp}\left\{X\left[3(g/g^*)^{2/3} - 2(g/g^*)\right]\right\} dg \,. \tag{23}$$

The above expression may be compared with Equation (11) obtained by Becker & Döring. The factor s_{g^*} on the left hand side, in place of s_1, arises as follows. In the Becker & Döring derivation, α_g is taken to be proportional to the vapour pressure over a drop of size g. Actually, this is only strictly correct when g is so large that the surface area of the drop may be considered constant for the evaporation or condensation of a single molecule. Actually from (17) and (21) it follows that

$$\frac{\alpha_g}{\beta_{g-1}} = \frac{s_{g-1}}{s_g}\,\frac{N_{g-1}}{N_g}$$

$$= \frac{s_{g-1}}{s_g}\,\mathrm{Exp}\left\{\frac{2\sigma M}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3}\left(g^{-1/3} - g^{*-1/3}\right)\right\} \tag{24}$$

instead of (6). If the continued product of terms like (24) is taken, the critical term (16) will be multiplied by a factor s_1/s_{g^*}.

The absence of the factor $\mathrm{Exp}\left\{-X(3g^{*-2/3} - 2g^{*-1})\right\}$ on the right hand side of (24) will also be noticed. The elimination of this factor is not due to any mathematical approximation made in the derivation, but arises from the different way in which the small molecular complexes are considered. In the Frenkel treatment, the surface energy of the complex is assumed to be adequately represented by the term $4\ r_g^{\,2}\sigma$, down to $g = 2$. In the Becker & Döring treatment, on the other hand, the Kelvin formula (1) is assumed to hold accurately for these small complexes. As already pointed out, it is unlikely that such simple assumptions can be made when the complex consists of a few molecules only.

Frenkel evaluates the integral in (23) in exactly the same way as Becker & Döring, and his final result is therefore in our notation

$$I = \frac{\beta_1 S_1}{g^{*\,1/3}} (X/3\pi)^{\frac{1}{2}}\ \mathrm{Exp}\ (-X) \quad . \qquad (25)$$

Rates of Drop Formation

To calculate the rates of drop formation at given conditions of supersaturation and temperature, the equations derived above may be written in more convenient forms. Using (5) for β_1 and taking $s_1 = 4\pi(3m/4\pi d)^{2/3}$, the total number of gas-kinetic collisions per cm^3 involving pairs of single molecules is approximately given by

$$\beta_1 s_1 \quad = \quad \frac{4\pi p^2}{(2\pi m)^{\frac{1}{2}}(kT)} \left(\frac{3m}{4\pi d}\right)^{2/3} \quad . \qquad (26)$$

The actual number of collisions will not differ from this by a significant amount. The use of (5) implies, however, that the condensation coefficient is unity, that is, all the molecules which collide are assumed to stick together for an appreciable time. This assumption is not necessarily true, and it is therefore possible that the actual value of β_1 may differ substantially from (5) *). It may be noticed that the condensation coefficient only appears in the formula for the condensation rate through β_1.

Using the above expression for $\beta_1 s_1$, and substituting for X from (9), the Becker & Döring expression for the condensation rate may be put into the form

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*) This point was kindly brought to my notice by Dr. G.A.P. Wyllie.

$$\ln I = \ln\left(\frac{2m\sigma}{\pi}\right)^{\frac{1}{2}}\left(\frac{p_\infty}{kT}\right)^2 \frac{1}{d} - \frac{2}{3}\ln g^* -$$

$$\frac{\sigma M}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3}\left(g^{*2/3} - 4g^{*-1/3}\right). \quad (27a)$$

As pointed out, if their assumptions are correct, it would be more accurate to retain the terms $3g^{*-2/3} - 2g^{*-1}$ in the exponential in (13). This leads to an alternative expression for the condensation rate

$$\ln I = \ln\left(\frac{2m\sigma}{\pi}\right)^{\frac{1}{2}}\left(\frac{p_\infty}{kT}\right)^2 \frac{1}{d} - \frac{2}{3}\ln g^* -$$

$$\frac{\sigma M}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3}\left(g^{*2/3} - 3 - 2g^{*-1/3}\right). \quad (27b)$$

The Frenkel expression for the rate of drop formation gives

$$\ln I = \ln\left(\frac{2m\sigma}{\pi}\right)^{\frac{1}{2}}\left(\frac{p_\infty}{kT}\right)^2 \frac{1}{d} - \frac{\sigma M}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3}\left(g^{*2/3} - 4g^{*-\frac{1}{3}}\right).$$

(27c)

These expressions for the condensation rates may be written directly in terms of the supersaturation and temperature, as follows. Introduce the parameter

$$x = \ln S \quad , \quad (28)$$

so that from (1)

$$x = \frac{2m\sigma}{dkT}\frac{1}{r^*} = \frac{2M\sigma}{dRT}\left(\frac{4\pi d}{3m}\right)^{1/3} g^{*-1/3}. \quad (29)$$

Substituting for g^* in (27a), and inserting numerical values for the physical constants, the rate of drop formation as predicted by Becker & Döring is found to be given by

$$\ln I = 57.5 + \ln(d^{1/3} p_{\infty}^{2})/(M^{5/6}\sigma^{3/2}) + 2x + 2 \ln x$$
$$-17.55(M/d)^2 (\sigma/T)^3 x^{-2} . \qquad (30a)$$

Alternatively, using (27b), the rate of drop formation becomes

$$\ln I = 57.5 + \ln(d^{1/3} p_{\infty}^{2})/(M^{5/6}\sigma^{3/2}) + 4.90(\sigma/T)(M/d)^{2/3}$$
$$+ x + 2 \ln x - 17.55(M/d)^2(\sigma/T)^3 x^{-2} .$$
$$(30b)$$

The Frenkel expression (27c) gives

$$\ln I = 59.9 + \ln (M\sigma)^{\frac{1}{2}}(p_{\infty}/T)^2/d \quad + 2x$$
$$-17.55(M/d)^2(\sigma/T)^3 x^{-2} \quad . \qquad (30c)$$

In the formulae (30), M is the gram molecular weight of the liquid, while p_{∞} is its saturation vapour pressure at T in mm mercury, and the other quantities are in the usual c.g.s. units.

To get an idea of the numerical magnitudes, the special case of water vapour at 261°K was considered. In this case, the equations became, respectively,

$$\ln I = 49.8 + 2x + 2 \ln x - 150.0\, x^{-2} \quad ; \qquad (31a)$$

$$\ln I = 59.9 + x + 2 \ln x - 150.0\, x^{-2} \quad ; \qquad (31b)$$

$$\ln I = 54.7 + 2x - 150.0\, x^{-2} \quad . \qquad (31c)$$

The three formulae therefore predict condensation rates that differ appreciably. By calculating the supersaturations corresponding to the same condensation rate, the results predicted by Equations (30) may be compared in a way which is in better accord with the usual observations in cloud chambers. Thus the supersaturations that correspond to a condensation rate of one drop per cm^3 per second, are respectively,

$$S = 5.68 \quad \text{(using 31a)} \quad ; \qquad (32a)$$

$$S = 4.68 \quad \text{(using 31b)} \quad ; \qquad (32b)$$

$$S = 5.02 \quad \text{(using 31c)} \quad ; \qquad (32c)$$

so that the formulae lead to substantially different results. In view of the uncertainty in the properties of the small molecular complexes, it is not possible at this stage to decide which formula should be preferred.

All three Equations (30) predict a similar variation of the condensation rate with supersaturation. In these equations the initial terms are only slowly varying functions of the supersaturation, compared with the last term. Hence the Equations (30) may all be written in the form

$$\ln I = \ln F - 17.55(M/d)^2(\sigma/T)^3 , \qquad (33)$$

where F is a factor which varies only slowly with supersaturation and temperature. Its value also depends on the particular liquid, and on which of the three Equations (30) chosen.

Discussion of Experimental Conditions

For a comparison of the above theories with the observed dropwise condensations in cloud chambers, the conditions of supersaturation and temperature in a chamber after a fast expansion must be carefully considered. After a sudden expansion the gas in the chamber heats up rapidly, so that the supersaturation drops quickly to a value at which the rate of drop formation becomes negligible. To estimate the total number of drops that will be formed in an expansion chamber, it is necessary to know how the temperature and supersaturation in the chamber vary with time.

The problem of the initial heating in a Wilson cloud chamber after a fast expansion, has been considered by Williams (1939). He showed that in the initial stages the heating of the gas by conduction from the walls will be negligible, except for a thin layer near the walls. The initial heating of the bulk of the gas in the chamber is due to the adiabatic compression as a result of the expansion of this boundary layer. The temperature T of the gas in the chamber, a short time t after an adiabatic expansion, is shown by Williams to be given by

$$T = T_2 + (T_1 - T_2)1.14(A/V)(\gamma - 1)(Kt/\rho_2 C_2)^{\frac{1}{2}} . \qquad (34)$$

Here ρ_2 is the density and K the thermal conductivity of the gas after the expansion, C_2 the specific heat at constant pressure and γ the ratio of specific heats of the gas, T_1 the initial temperature and T_2 the temperature immediately after the expansion, V the volume of the chamber after expansion and A its surface area.

Since the diffusion coefficient is of the same order of magnitude as the coefficient of heat diffusivity, it follows that in the initial stages the loss in vapour due to diffusion to the walls will be negligible. The amount of vapour can therefore be considered constant and the supersaturation easily calculated from the temperature. The rate of drop formation as a function of time can then be evaluated from (33) and the total number of drops formed per cm^3 calculated from

$$N_o = \int_o^\infty F \exp\left\{-17.55(M/d)^2(\sigma/T)^3\right\} dt. \quad (35)$$

This procedure will be valid provided the number of drops formed are small enough for the effects of heat of condensation liberated by the drops and the vapour removed by them, to be negligible. The conditions under which this is true will be examined later.

To get an idea of the order of magnitude of the effective time for which the supersaturation lasts, the following typical example was considered. Air at an initial pressure of 600 mm mercury and temperature 293.7°K was expanded to 1.345 times its original volume. Assuming the expansion to be adiabatic, this results in a final temperature of 260.8°K and a nominal supersaturation of 6.30. The calculated rate of drop formation as a function of time, is shown by the full curve in Fig. 1, for a cloud chamber of size V/A = 1 cm. The constant I_o in the figure is

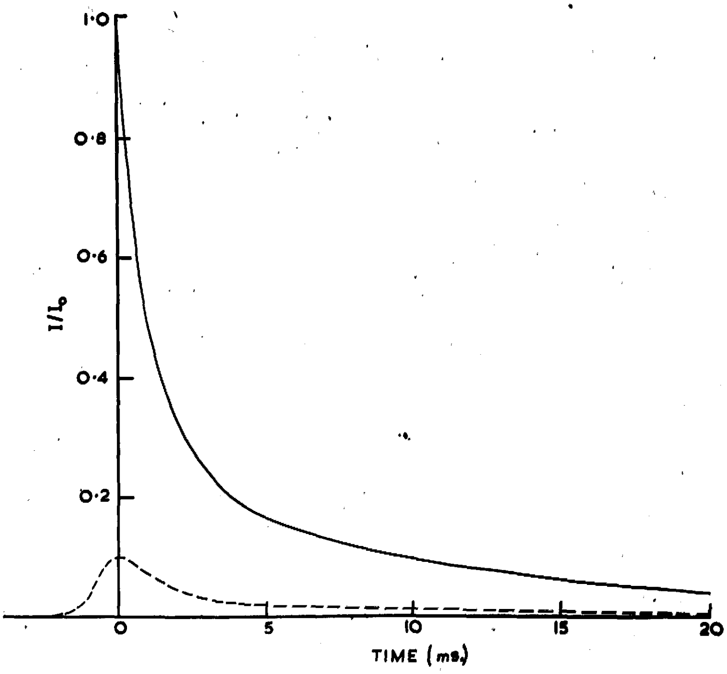


Figure 1. Variation of the fractional condensation rate, I/I_o, with the time after expansion for a typical cloud chamber (V/A = 1cm). Full curve, adiabatic expansion; broken curve, expansion of duration 0.01 seconds.

the rate of drop formation corresponding to the temperature T_2 and the nominal supersaturation S_2. The variation of condensation rate with time for a chamber of arbitrary size can be deduced from Fig. 1 by noting that according to (34), the time required for the gas in a chamber of 'size' V/A to reach the same temperature will simply be multiplied by a factor $(V/A)^2$. The total number of drops for a chamber of size $V/A = 1$ cm, is seen from Fig. 1 to be of the order of $0.005I_0$. In a chamber of arbitrary size the number of drops formed with the above conditions will therefore be $0.005\ (V/A)^2\ I_0$.

This estimate for the number of drops has still to be corrected for the fact that actual expansions are not adiabatic, but take a finite time τ. This means that the minimum temperature T_2' and the maximum supersaturation reached, will be different from the calculated nominal values. An approximate estimate of the maximum rate of condensation can be made as follows. As pointed out by Williams, the temperature distribution in the boundary layer after an expansion of duration τ will be approximately the same as that at a time $\tau/2$ after an adiabatic expansion. Hence the minimum temperature reached will be given by

$$T_2' = T_2 + 1.14(T_1 - T_2)(A/V)(\gamma - 1)\ (K\tau/2\rho_2 C_2)^{\frac{1}{2}} \tag{36}$$

The corresponding supersaturation and hence the maximum rate of condensation can be found as before.

Consider for example the case in which a chamber under the same initial conditions as above, is expanded to 1.345 times its initial volume in 0.02 sec. For a chamber of size $V/A = 1$ cm, it will be seen from the full curve in Fig. 1 that after a time $\tau/2 = 0.01$ sec., the condensation rate is approximately reduced to $0.1\ I_o$. Hence the condensation rate will probably vary as shown by the broken curve in Fig. 1. For a chamber of this size, the total number of drops formed per cm^3 will therefore be of the order of $0.001\ I_o$. Estimates of the total number of drops formed in chambers of different sizes and different expansion times, can be made in the same way. In Table 1 the variation of the number of drops with chamber size and expansion time, is shown in terms of the variable t_e, which is defined as

$$t_e = N_o/I_o \quad , \tag{37}$$

and which is therefore the effective duration of the supersaturation at its nominal value S_2.

Table 1. Effective Duration of Supersaturation.

τ (ms.)	V/A (cms)	t_e (ms.)
20	2.0	10
20	0.5	0.1
20	1.0	1
10	1.0	2
50	1.0	0.3

The method used above to estimate the total number of drops formed after a fast expansion will only be valid if the time interval for which the supersaturation remains essentially constant, is long enough for the equilibrium distribution to be set up. This can be shown to be the case in the present instance, from the following simple consideration. The stationary distribution will be set up when the vapour molecules have made sufficient collisions. Now a complex of g molecules is bombarded by βs_g

vapour molecules per second. Considering for example the case of water vapour at 261°K and a supersaturation of 6.3, a complex of g molecules makes about $4 \times 10^7 \ g^{2/3}$ collisions per second with single molecules. As there are only of the order of a hundred molecules in the equilibrium drop, it follows that the stationary distribution will be set up in a time which is certainly less than 0.1 ms. Since the supersaturation does not vary appreciably in this time, the stationary distribution can therefore be used in calculating the total number of drops.

It has also been assumed that the number of drops formed is not sufficient for the heat of condensation liberated and the vapour removed by the drops to affect the supersaturation significantly. An approximate estimate of the maximum drop density for which this assumption still holds, can be made by considering the growth of the drops.

The complete theory of the growth of a drop in a supersaturated vapour is very complicated, but Hazen (1942) has made several simplifying assumptions and derived expressions which are sufficiently accurate for the present purpose. In this calculation it is assumed that the drop has reached its equilibrium temperature T_d, when the gain in heat by condensation is exactly balanced by the loss due to conduction. The variation of the coefficients of diffusion of the vapour D and heat conductivity of the gas K, with temperature and density is neglected. The drop is considered to be large enough for the effect of surface tension on the equilibrium vapour pressure to be negligible, so that the pressure just round the drop is equal to $p_\infty(T_d)$, the saturation vapour pressure at T_d. Finally, the effect of the motion of the drop through the vapour is neglected.

Under these conditions it is found that at a given supersaturation and temperature the surface area of a drop increases linearly with time. This rate of increase is determined by two simultaneous equations for the unknowns dr^2/dt and T_d,

$$\frac{dr^2}{dt} = \frac{2DM}{Rd}\,(p/T - p_\infty(T_d)/T_d) \ , \qquad (38)$$

$$\frac{dr^2}{dt} = \frac{2K}{Ld}\,(T_d - T) \ , \qquad (39)$$

where r is the radius of the drop after time t, and L the latent heat of condensation. It was found by

Hazen (1942) and by Barrett & Germain (1947) that these formulae represent the observed growth of drops in nitrogen and air fairly well.

Using these expressions, the following estimate can be made for the drop density at which the condensation will start to affect the supersaturation. Suppose that in an interval t seconds, the total number of drops formed per cm^3 is N_t. Then the decrease in the vapour density will be less than that produced by N_t drops formed at the beginning of the interval and growing at the maximum rate (the rate corresponding to the maximum supersaturation at the beginning of the interval). Hence, if ρ is the vapour density and $-\Delta\rho$ the decrease in vapour density in time t, then

$$-\frac{\Delta\rho}{\rho} < \frac{4\ r^3 d\ N_t}{3} \quad . \tag{40}$$

An upper limit for the average increase in gas temperature ΔT due to the latent heat, is similarly given by

$$\Delta T < \frac{4\ r^3 dLN_t}{3} \quad . \tag{41}$$

As an example of the magnitude of N_t at which the effect of condensation becomes noticeable, the case of water vapour at 261°K and an initial supersaturation of 6.30, was again considered. The solutions of Equations (38) and (39) in this case is

$$dr^2/dt = 3.6 \times 10^{-6} \text{ cm}^2/\text{sec.} \quad ,$$

$$\text{or} \quad r = 1.9 \times 10^{-3} \, t^{\frac{1}{2}} \text{ cm.} \tag{42}$$

Substituting this value for r in (40) and (41), and inserting numerical values, they become respectively

$$-\Delta\rho/\rho < 2.3 \times 10^{-3} \, N_t \, t^{3/2} \quad , \tag{43}$$

$$\Delta T < 1.1 \times 10^{-2} \, N_t \, t^{3/2} \quad . \tag{44}$$

Now from Fig. 1 it has been found that in a chamber of size V/A = 1 cm, most of the condensation takes place in an interval of 0.01 sec. Using this value for t in (43) and (44), these equations become

$$-\Delta\rho/\rho < 2.3 \times 10^{-6} \, N_t \quad , \tag{45}$$

$$\Delta T < 1.1 \times 10^{-5} \, N_t \quad . \tag{46}$$

It can therefore be concluded that in this case the effect of the heat of condensation and removal of vapour , will be small at drop densities as high as 10^4 per cm^3. At substantially higher drop densities it is of course necessary to take into account these effects, as done by Mason (1951).

Conclusion

By considering the fluctuations that may occur in a supersaturated vapour, it has thus been possible to derive expressions for the rate of drop formation in the absence of contaminating nuclei. The difference in the expressions arises from the different ways in which the properties of small drops are considered. All the existing theories, however, assume certain properties of large drops to apply also to small aggregates of vapour molecules. Although this assumption is not necessarily valid, it has previously been considered that the small complexes would not have a large influence on the rate of drop formation. It has been pointed out above that this consideration is wrong, and that the small drops do control the condensation. In order to get a more accurate estimate of the rate of condensation, it is therefore necessary to have a more detailed knowledge of the properties of small molecular complexes. Until such knowledge becomes available, either from experiments on condensation, or from theoretical considerations, the expressions for the condensation rate must be regarded as first approximations only.

Since the condensation rate varies so rapidly with supersaturation, the effective time for which the supersaturation persists after a fast expansion, is very short. This consideration must be taken into account when the expressions for the condensation rate are compared with the number of drops observed after a fast expansion. In Part II some observations in cloud chambers will be compared with the theoretical predictions. Before proceeding, however, a brief indication will be given of how the theory has to be modified when the condensation takes place on ions.

CONDENSATION ON IONS

The equilibrium radius r of a drop of liquid carrying a charge e, is given by the J.J. Thomson (1888) equation,

$$\ln \frac{p}{p_\infty} = \frac{M}{RTd}\left\{\frac{2\sigma}{r} - \frac{e^2}{8\pi r^4}\right\} . \qquad (47)$$

The variation of r with vapour pressure is illustrated in Fig. 2. It will be seen that at relatively small

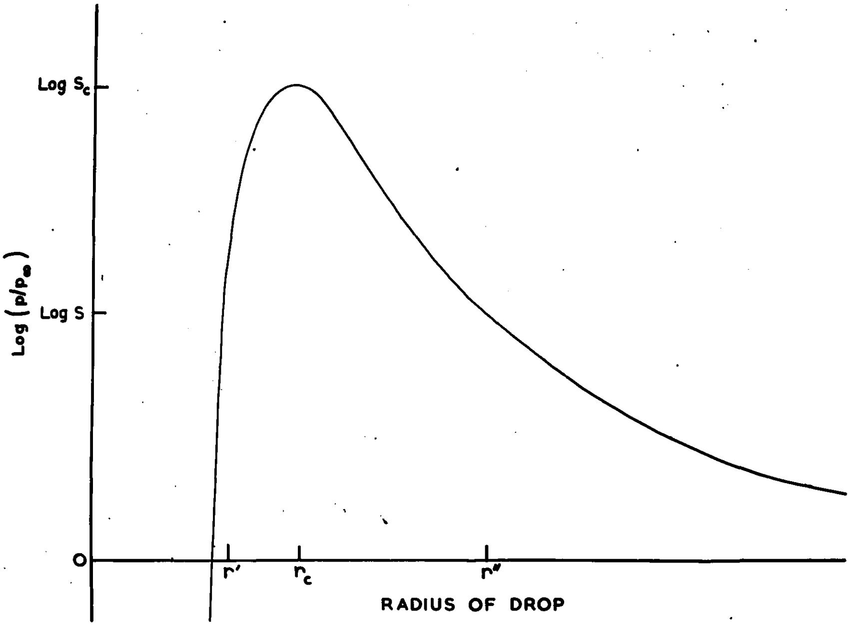


Figure 2. Variation of the equilibrium vapour pressure over a charged drop with the radius.

supersaturations there are two values of r satisfying Equation (47), of which the smaller radius r' corresponds to a stable equilibrium and the larger radius r" to an unstable equilibrium. According to the simple theory the equilibrium vapour pressure must always be less than a maximum value p_c. If the vapour pressure exceeds this value, then the vapour will be supersaturated with respect to all ions, and they should grow to visible size. This vapour pressure p_c, corresponding to a supersaturation S_c, is found from (47) to be given by

$$\ln S_c = \ln \frac{p_c}{p_\infty} = \frac{2M\sigma}{RTd} \left(\frac{4\pi\sigma}{e^2}\right)^{1/3} . \qquad (48)$$

It can be expected, however, in analogy with the formation of uncharged drops by fluctuations, that even at lower vapour pressures there will be a chance that the radius of some ion will fluctuate from r' to visible size. The probability of this happening will increase with increasing supersaturation, so that at a certain supersaturation, depending on the ion density, condensation will start to become observable.

This is in accordance with the observations in cloud chambers. There is found to be a gradual transition from the point where condensation on ions just becomes noticeable to the limit where all the ions cause condensation. As the supersaturation where condensation on ions just sets in, is easier to determine experimentally, most measurements are given in terms of this so-called 'critical supersaturation' for ion condensation. A fact which is often overlooked is that the limit depends of course slightly on the ion density.

In Table 2, given by Scharrer (1939), the values of S_c for different liquids are compared with the measured critical supersaturations, using X-Rays to ionize the gas. As expected, all the observed supersaturations are less than that predicted by (48), with however the notable exception of methyl alcohol. This anomolous behaviour of methyl alcohol as regards ionic condensation as well, is very difficult to understand, and no satisfactory explanation of the effect has yet been given.

Table 2. Critical Supersaturations for Condensation on Ions (from Scharrer)

Liquid	Observed Supersat.	S_c
Water	4.14	4.64
Ethyl Alcohol	1.94	2.52
Methyl Alcohol	2.95	2.07
Benzene	4.94	11.4
Carbon Tetrachloride	6.0	12.7
Chloroform	3.4	7.4
Chlorobenzene	8.9	30.0

Tohmfor & Volmer (1938) have extended the condensation theory of Becker & Döring to condensation on ions, in this case assuming Equation (47) to hold accurately even for small complexes. They again consider the stationary state in which a supersaturated vapour is enclosed in a large container with Z ions per cm^3. Drops form and grow and they are removed as soon as they reach a sufficiently large size. The loss in vapour and ions is continuously replenished.

Under these conditions, the number of drops formed per cm^3 per second was found to be

$$I_z = \frac{m\beta r'^2}{r''^3 d}\left\{\frac{4\pi o r''^2 - e^2/r''}{kT}\right\}^{\frac{1}{2}} \quad x$$

$$\mathrm{Exp}\left\{-\left[4\pi o(r''^2 - r'^2) - 2e^2(r'^{-1} - r''^{-1})\right]/3kT\right\} \tag{49}$$

Tohmfor & Volmer compared expression (49) with the observation of Wilson (1899) who measured the critical supersaturation for condensation on ions to be 4.1 for water at 267.9°K. Assuming Z to be 10^3, Equation (49) predicts a condensation rate of 10^{10} drops per cm^3 per second. As shown previously, the condensation rate used by Wilson was probably at least as high as 10^4. Even so, the discrepancy is far in excess of the uncertainty in the value of Z and of the condensation rate.

Tohmfor & Volmer gave the following explanation for the discrepancy. They pointed out that for a charged drop of dielectric constant ε_1 surrounded by a gas of dielectric constant ε_2, Equation (47) should be modified to

$$\ln \frac{p}{p_\infty} = \frac{M}{RTd}\left\{\frac{2\sigma}{r} - \left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right)\frac{e^2}{8\pi r^4}\right\} . \qquad (50)$$

If the bulk values of $\varepsilon_1 = 80$ for water and $\varepsilon_2 = 1$ for air are substituted in (50), the equation reduces in practice to the Thomson equation. Tohmfor & Volmer point out, however, that the molecules in the small drop of radius r' are in the strong electric field of the charge, so that as a result of the orientation of the dipole moments of the molecules, the dielectric constant for such a drop may be substantially less than the bulk value. Actually a value of $\varepsilon_1 = 1.85$ for water is required to give agreement with the experimental condensation rate. Whatever the detailed explanation of the effect, it is clear that the behaviour of the small complexes may be widely different from that of small drops of ideal liquid.

A detailed theory of condensation on ions will also have to take into account the effect first observed by Wilson (1900) that negative and positive ions differ in efficiency as condensation nuclei. Thus Wilson found that in water vapour the condensation started to take place on the negative ions at a supersaturation of 4.1, while the corresponding value for positive ions was found to be 5.2. Laby (1908) studied the effect in organic liquids and found that these liquids condensed preferentially on the positive ions. More recently, Scharrer (1939) has repeated the experiments and found that for water and chlorobenzene the condensation took place more easily on the negative ions, while for methyl and ethyl alcohol and to a smaller extent chloroform, the positive ions were more efficient condensation nuclei. No difference between the positive and negative ion condensation could be detected with benzene and carbon tetrachloride. The above effect is not predicted by either the simple Thomson theory or the more detailed treatment of Tohmfor & Volmer, and no completely satisfactory explanation of it has yet been given.

PART II

EXPERIMENTS ON THE CONDENSATION OF VAPOURS IN THE ABSENCE OF CONTAMINATING NUCLEI

INTRODUCTION

Since the classical researches of C.T.R. Wilson (1897, 1899), the condensation of vapours in the absence of ions has been studied by many workers. The previous investigations will be briefly reviewed in the following section, where it will be pointed out that the results obtained are not sufficient for an adequate comparison with the theory developed in Part I. The previous experiments usually suffer from the defect that the condensation rates corresponding to the experimental conditions, are not clearly defined.

There is thus clearly a need for some experiments in which the considerations regarding the effective duration of the supersaturation, are duly taken into account. This Part describes some experiments on the condensation of water vapour, in which the drop density was determined as a function of the expansion ratio. This enabled a fuller comparison with the theory. Experiments were also done with a small cloud chamber and with different liquids.

REVIEW OF PREVIOUS EXPERIMENTAL WORK

The Experiments of Wilson

The classical series of experiments on the subject of condensation was done by C.T.R. Wilson (1897, 1899). Wilson observed that when dust free air, saturated with water vapour, was expanded adiabatically, then condensation would take place if the expansion ratio exceeded 1.25. Comparatively few drops were formed, however, provided the ratio was less than 1.38. These drops were ascribed to condensation on ions naturally present in the gas. When the ratio was increased beyond 1.38, a sharp increase in the number of drops was observed, dense clouds resulting from expansions slightly exceeding the above ratio. The supersaturation at this so-called 'cloud limit' was independent of the permanent gas used, and Wilson suggested that the cloud was caused by condensation of the vapour molecules on aggregates of themselves.

Wilson's original investigation is not well suited for comparison with the theory of condensation, since the rate of condensation corresponding to his cloud limit is uncertain. Furthermore, the drop densities involved might have been large enough for the latent heat liberated by the drops to affect the condensation and thus complicate the interpretation.

Investigation of Andren

Andren (1917) studied the variation of drop density with expansion ratio in different vapours. At low drop densities the number of drops was simply estimated visually. When the separate drops could no longer be resolved, the drop density was estimated indirectly from the rate of fall of the cloud and the expansion data. Both these methods of determining the drop density are only very approximate. Andren interpreted his results in terms of the earlier theory of condensation proposed by Lenard (1914), in which the condensation was assumed to take place on nuclei consisting of relatively stable complexes of the vapour molecules.

Measurements of Powell

Powell (128) has measured the expansion ratios corresponding to the cloud limit for water at various temperatures. For these experiments a small expansion chamber was used, and the nominal final temperature ranged from 47°C to -26.4°C. The expansion ratio necessary for the production of a cloud was observed to decrease with increase in temperature. The corresponding variation in the supersaturation with temperature was recently compared by Farley (1952) with that expected from the Becker & Döring (1935) theory, and found to be only in approximate agreement.

The observations of Powell are again not suitable for comparison of the absolute condensation rate with theory, as the drop density corresponding to the cloud limit is uncertain. Furthermore, the heat of condensation liberated at the cloud limit, may have had an appreciable effect on the drop formation.

Measurements of Volmer & Flood

Volmer & Flood (1934) made a careful study of the condensation of different vapours in the absence of contaminating nuclei, determining for each a 'critical expansion ratio'. This was defined as the expansion ratio which was such that a small increase in the ratio just produced a noticeable increase in the number of drops over the background due to spray.

They compared their results with the expression for the condensation rate derived by Volmer & Weber (1926) and Farkas (1927) from thermodynamical arguments. The expression used by Volmer & Flood is equivalent to Equation (33) in Part I,

$$\ln I \;=\; \ln F \;-\; 17.55(M/d)^2(\sigma/T)^3\, x^{-2}\,, \qquad (1)$$

where F was considered to be a constant for the different liquids. I is the number of drops formed per cm^3 per second, M is the molecular weight, d the density and σ the surface tension of the liquid, T the temperature and $x = \ln S$, S being the supersaturation. Using Equation (1), the supersaturations for different liquids corresponding to the same condensation rate I, could be calculated. The constant F was chosen so as to give the 'critical supersaturation' for water vapour at 264°K to be 4.85, in agreement with the observed value. The calculated supersaturations are compared with the measured values in Table 1.

Table 1. Critical Supersaturations (Volmer & Flood)

Liquid	T_2(°K)	Supersaturation	
		Theor.	Exp.
Water	264	(4.85)	4.85
Water	275.2	4.30	4.21
Methyl Alcohol	270	1.84	3.20
Ethyl Alcohol	273	2.30	2.34
n-Propyl Alcohol	270	3.20	3.25
Isopropyl Alcohol	265	2.90	2.80
Butyl Alcohol	270	4.50	4.60
Nitromethane	252	6.25	6.05
Ethylacetate	240	11.0	12.3

The variation of the critical supersaturation for water vapour with temperature, was in good agreement with the theoretical predictions. For all the other liquids, with the notable exception of methyl alcohol, the observed critical supersaturation was found to be in good agreement with the calculated value.

The above measurements of the critical supersaturations were compared by Becker & Döring (1935) with their expression for the rate of drop formation (equivalent to Equation (30a) in Part I). They took the measured critical supersaturation to correspond to a rate of drop formation of 1 drop per cm^3 per second, as given by Volmer & Flood. For water at $261^{\circ}K$, for instance, the supersaturation corresponding to this condensation rate was calculated to be 5.14, in good agreement with the measured value of 5.03.

The condensation rate given by Volmer & Flood seems rather low. It has been estimated (see Table 1, Part I) that in their chamber ($V/A = 2$ cm) the effective duration of the supersaturation would be of the order of 0.01 seconds. Now a drop density of the order of about 1 per cm^3 would perhaps just be noticed above the background, so it is probable that the condensation rate used by Volmer & Flood was of the order of 100 drops/cm^3second. On the Becker & Döring theory, this condensation rate corresponds to a supersaturation of 5.5.

Observations of Scharrer

Scharrer (1939) measured the 'critical expansion ratios' for a variety of liquids, using the same criterion as Volmer & Flood to define the critical ratio. He obtained good agreement with Volmer & Flood for water, ethyl alcohol and methyl alcohol. Other liquids investigated by Scharrer were benzene, carbon tetrachloride, chloroform and benzene chloride. The rate of drop formation corresponding to the 'critical ratio' used by Scharrer, is again not clearly defined.

Experiments of Frey

By photographing and counting the drops formed with water vapour in a small cloud chamber, Frey (1942) studied the variation in the drop density with expansion ratio. With increasing ratio, the drop density was observed to increase rapidly at first, but soon the increase became slower, and finally (at a drop density of about $10^6/cm^3$) no further increase with the expansion ratio could be observed.

Frey interpreted his results in terms of the early condensation theory of Lenard (1914), considering that at large expansions, drops were formed on all the 'nuclei' (visualized by Lenard as relatively stable complex molecules). Recently, Mason (1951) has shown, however, that the limiting drop density can be explained simply in terms of the Becker & Döring theory, when the heat liberated by the condensation is taken into account. At large drop densities, the latent heat of condensation of the drops formed even before the end of a fast expansion, has the effect of limiting the effective duration of the supersaturation. It can therefore be expected that at large expansion ratios, no further increase in the drop density will be observed. At the high drop densities used by Frey, (he could not measure drop densities below about

$10^3/cm^3$), the heat liberated by the condensation complicates the interpretation of his results.

Frey estimated that a drop density of $1/cm^3$ would correspond to a supersaturation of 4.9 and a final temperature of 263°K. This supersaturation is rather lower than would be expected from the measurements of Volmer & Flood, considering the fact that Frey used a small chamber ($V/A = 0.5$ cm). Frey's procedure is, however, open to the criticism that the cleaning of his chamber was not adequate. Since the chamber was not completely sealed off, he attempted to clean the chamber before each expansion by irradiating with X-Rays while continuously applying an electric field. It is clear that this method would not remove the larger drops and dust particles in a reasonably short period.

Conclusion

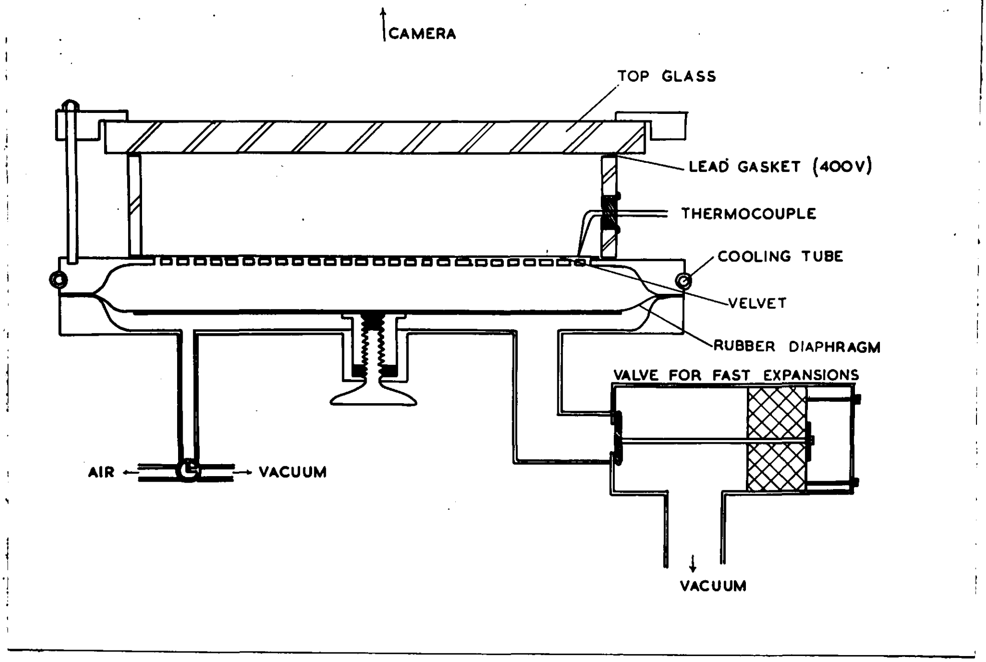
It can therefore be concluded that the above measurements on the condensation of liquids are not sufficient for an adequate comparison with the theory. There is thus a need for further experiments in which the effective duration of the supersaturation is carefully estimated to get a more accurate determination of the condensation rate. For an accurate measurement of the drop density, a photographic technique seems desirable. The experiments should, however, be done at drop densities which are low enough for the heat of condensation to have a negligible effect on the drop formation.

CONDENSATION OF WATER VAPOUR

The condensation of water vapour was studied experimentally by determining the number of drops formed at different expansion ratios. In this way a more reliable comparison could be made with the theory of condensation.

Apparatus

The cloud chamber used for the experiment was of the rubber diaphragm type, and is illustrated diagrammatically in Fig. 1. The water was contained on a velvet cloth, which also served as a photographic



<u>Figure 1.</u> Diagram of large expansion cloud chamber.

background. The usual arrangements were made for the slow and fast expansions. A potential of 400 V was continuously applied to the lead wire serving as gasket between the cylinder and the top glass plate.

The illumination for photography was supplied by two flash lamps, on discharging a total capacity of 300 μF charged to a potential of 2 kV, through each of them. The discharge was initiated by the spark from the secondary of an ignition coil, the primary of which was excited by the discharge from a 4 μF condenser charged to 300 V. The instant of discharge could be delayed to take place at a convenient time after the expansion, by means of a thyratron circuit. The chamber was photographed with a 60 mm camera, so constructed that after development the film could be replaced in the camera and image projected on to a screen. The light from the lamps was carefully collimated into a narrow beam of width 0.5 cm.

To keep the top glass plate clear from condensation, it was necessary to cool the bottom of the chamber by circulating water round the base. In order to measure the temperature of the chamber while the experiment was in progress, a thermocouple was fixed through a window in the cylinder, so that the joint just touched the velvet.

Precautions

For precision measurements, it is necessary to determine the temperature conditions inside the chamber accurately. The temperature gradient inside the chamber set up by the cooling coil was measured with a thermocouple. It was found that under normal operating conditions, the temperature gradient in the chamber was approximately constant, the top being 2°C hotter than the base. The mean temperature of the gas in the chamber was therefore taken to be 1.0°C above the temperature of the vapour source indicated by the fixed thermocouple.

Before a fast expansion is made, it is necessary to ensure that the temperature and vapour pressure in the chamber has come to equilibrium after the preceding compression. The temperature variation after a compression was therefore studied using a thermocouple suspended in the centre of the chamber. Fig. 2 shows the observed variation in temperature under

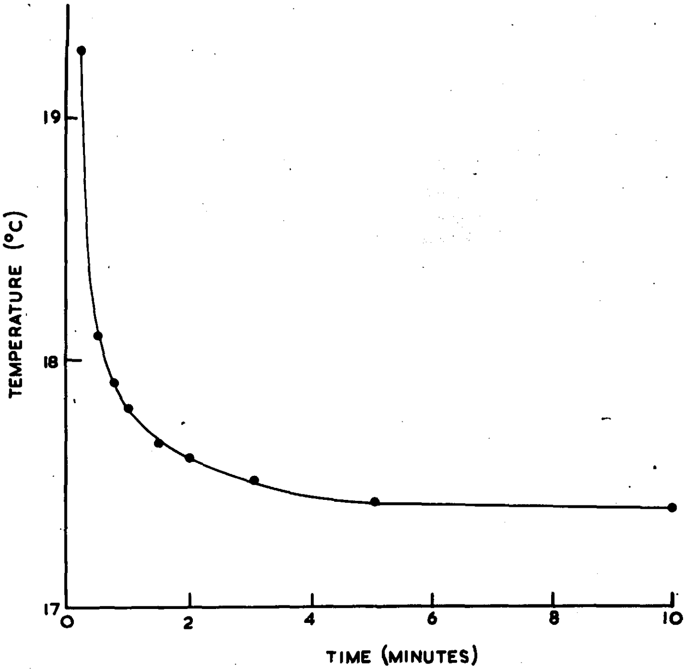


Figure 2. Temperature variation in the large expansion chamber after a compression.

normal running conditions. It will be seen that it takes at least three minutes for the temperature to reach within 0.1°C of its equilibrium value. For the measurements of drop density it was therefore decided to wait three minutes after the preceding compression before making a fast expansion. This delay could not be increased, since otherwise the series of expansions would take too long for the temperature to stay reasonably constant. As the coefficient of heat diffusivity is of the same order of magnitude as the diffusion coefficient, it can be expected that the vapour pressure in the chamber will also reach a sensibly constant value in 3 minutes.

Procedure

To eliminate the effect of a systematic variation in the temperature of the chamber, the expansions were made with the ratio increasing in small steps, until a cloud could be seen, when the ratio was again decreased by the same steps. After each expansion the chamber was carefully cleared by a series of slow expansions, and an interval of 3 minutes allowed to elapse before making the next fast expansion. The temperature of the velvet was read at frequent intervals. In order to distinguish separate drops, it was found necessary to delay the illuminating flash about 0.15 seconds after the expansion.

After development, the film was replaced in the camera, and the image projected on to a screen. Fig. 3 shows a section of the chamber that was found suitable for counting the drops. Since the illumination varied over the chamber area, the same regions (of total area 10 cm^2) were selected for the drop counts at different expansions.

Results

The results of a typical series of expansions are shown in Table 2. Figure 4 shows the variation in the mean number of drops with expansion ratio.

At drop densities below about 10 per cm^3, the estimate of the number of drops formed on molecular aggregates, became inaccurate, due to the occurrence of a few stray drops per cm^3. On the other hand, at drop densities above about $500/cm^3$, it became difficult to distinguish individual drops. The observed variation in the number of drops at the same expansion

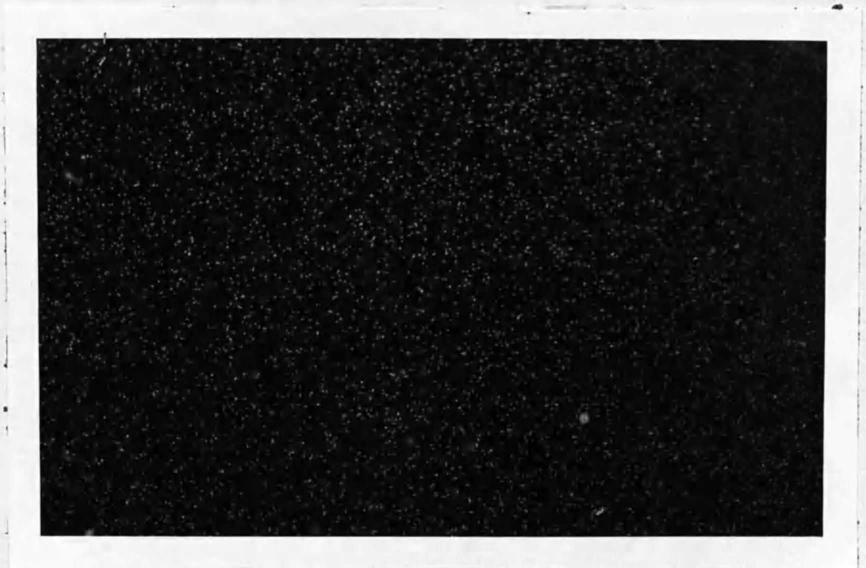


Figure 3. Section of cloud chamber suitable for drop counting.

ratio is probably due to small variations in the initial conditions in the chamber.

Table 2. Drop Densities at Different Expansion Ratios (Water vapour & air, initially at 20.7°C)

Expansion Ratio	Drop Density (N_o)			$\log_{10}N_o$
	Ratio Inc.	Ratio Decr.	Mean	
1.318	10.8	10.1	10.5	1.03
1.323	22.3	13.4	18.4	1.24
1.329	51.6	30.2	41	1.60
1.334	121	151	136	2.13
1.340	351	341	346	2.54
1.345	730	547	639	2.80

Interpretation of Results

It has been pointed out in Part I that all the expressions for the condensation rate can be written in the form of Equation (1),

$$\ln I = \ln F - 17.55\,(M/d)^2(\sigma/T)^3\,x^{-2}\,. \qquad (1)$$

The total number of drops formed after an expansion

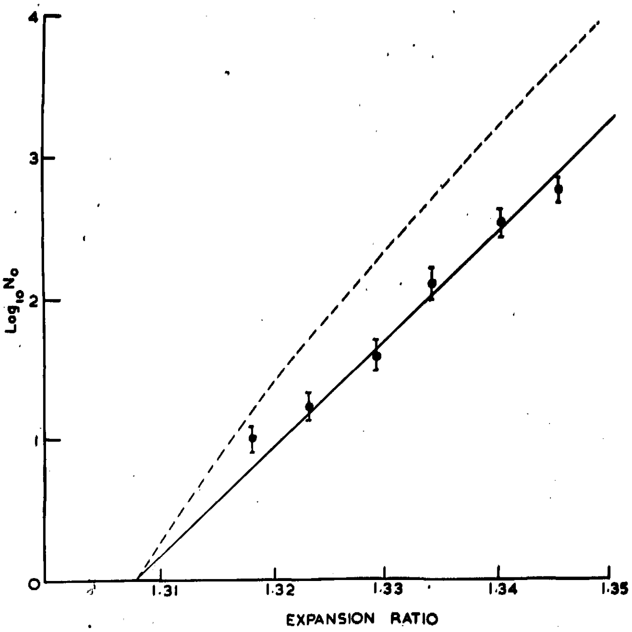


Figure 4. Variation of drop density with expansion ratio. Full line, observed values; broken line, calculated variation.

may be written as

$$N_o = I_o t_e \quad , \tag{2}$$

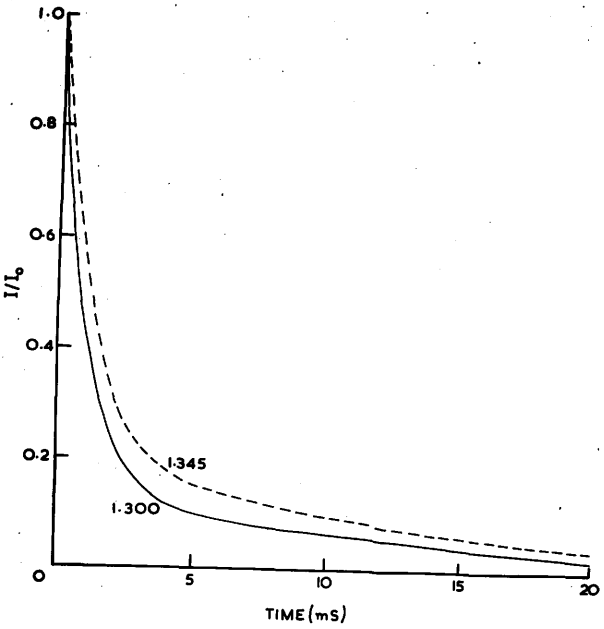
where t_e is the effective duration of the supersaturation at its nominal value, calculated from the expansion data, and I_o is the corresponding nominal rate of condensation.

Assuming that both the factors F and t_e remain effectively constant over the range of expansion ratios used, the number of drops can then be calculated as a function of the expansion ratio. This is done in Figure 4, where the constants F and t_e were chosen so as to give agreement with the observations at a drop density of $1/cm^3$.

It will be seen from Figure 4 that the increase in the number of drops with expansion ratio is less rapid than predicted by the theory. The discrepancy lies outside the experimental errors caused by variations in the initial conditions. It was also checked that the discrepancy is not introduced by the simplifying assumption that both F and t_e may be considered constant over the range of expansion ratios used. To study the variation in the effective time t_e, the rate of drop formation was calculated as done in Part I, for adiabatic expansions of 1.300 and 1.345, with the same initial conditions as existed in the experiment, and for a chamber of size V/A = 1 cm. The resultant variation in I, the rate of condensation, is shown in Figure 5. It will be seen that the larger expansion ratio actually corresponds to a slightly larger time t_e. Thus the more rapid heating of the chamber at the larger ratio is more than compensated by the slower decrease in the resulting rate of drop formation. It can also be expected that the variation in the duration of the expansion, will produce only a small variation in t_e.

It was also verified that the variation in F given by the more elaborate Equations (30) in Part I, could not account for the discrepancy. Thus for instance, the Becker & Döring formula (30a) leads to an increase in $\log_{10}F$ of 0.3 over the above range of expansion ratios. This increase in the term F will further enlarge the discrepancy between the theory and experiment.

It will be seen from Figure 5 that a drop density of $1/cm^3$ occurred at an expansion ratio of 1.308 ± 0.005. This corresponds to a nominal supersaturation of



<u>Figure 5.</u> Variation in condensation rate with time after different adiabatic expansions, for a typical cloud chamber (V/A = 1 cm), initial temperature 20.7°C.

5.20 ± 0.15 and a final temperature of 263.7°K. This result may be compared with the critical supersaturation of 4.85 observed by Volmer & Flood for water vapour at 264°K. They used a fairly large chamber for which the effective duration of the supersaturation was estimated to be about 5 times longer than in the chamber used for the above experiments. Their critical supersaturations thus seem to indicate that they had actually worked with a drop density of $1/cm^3$, rather than with a condensation rate of 1 drop per cm^3 per second.

Table 3 shows the drop densities calculated from Equations (30) in Part I, corresponding to the observed supersaturation and temperature, assuming $t_e = 10^{-3}$ sec. It will be seen that the Frenkel formula gives the best agreement with the observations.

Table 3. Drop Densities from Different Equations

Equation	$\log_{10} N_o$
(30a) Becker & Döring	-1.96
(30b) More accurate	+1.34
(30c) Frenkel	-0.22

Conclusions

It may thus be concluded that the condensation of water vapour is in approximate agreement with the theory discussed in Part I. A detailed interpretation of the results cannot, however, be made in terms of the present theory. In particular, the increase in drop density with expansion ratio is not in satisfactory agreement with the theory which assumes some properties of large drops also to hold for small molecular complexes. A further study of the increase of drop density with expansion ratio may give valuable information about the properties of small aggregates of molecules.

The experimental results are in good agreement with those of Volmer & Flood (1934) and Scharrer, assuming that the 'critical supersaturations' of these workers actually corresponded to a drop density of about $1/cm^3$. Recently Farley (1952) has stated that the results of Volmer & Flood and Scharrer are not in agreement with the earlier observations of Wilson (1899) and Powell (1928). Thus Wilson reported only a rainlike condensation if the expansion ratio did not exceed 1.38, at which value dense clouds was observed. It seems reasonable to assume, however, that Wilson observed a rather more sudden transition than later workers because he increased the expansion ratio in larger steps. There does however exist the possibility that in larger chambers, contaminating substances may be introduced by the rubber and the velvet, for instance.

It was therefore decided to repeat the condensation experiments in a small cloud chamber, in which a higher standard of purity could be attained, to see if it shows any difference in behaviour which cannot be explained simply in terms of the more rapid heating of the gas in the chamber.

EXPERIMENTS WITH SMALL CLOUD CHAMBER

The cloud chamber used for these experiments was of essentially the same design as that used by C.T.R. Wilson in his original investigation. It was so constructed that only glass and the liquid under investigation came into direct contact with the working volume of the chamber. The small cloud chamber could be cleaned quite readily, and was therefore also suitable for the study of condensation in different liquids.

Apparatus

A diagram of the chamber with mechanism for slow and fast expansions is shown in Fig. 6. The chamber consisted essentially of an inverted test tube, of internal diameter 2.5 cms. The small glass piston moved inside this tube, the ends of the piston being ground flat. To expand the chamber, the space underneath the piston was evacuated, so that the piston was sucked down, coming to rest squarely on the rubber stopper closing the end of the tube. The expansion ratio was varied by changing the volume of gas above the piston by means of the manometer reservoir connected to the chamber through a capillary tube and tap. The expansion ratio was estimated from the stroke of the piston, the effective length of the chamber in the expanded position being 9.70 cms. This method of determining the expansion ratio was found to be more convenient than that used by Wilson,

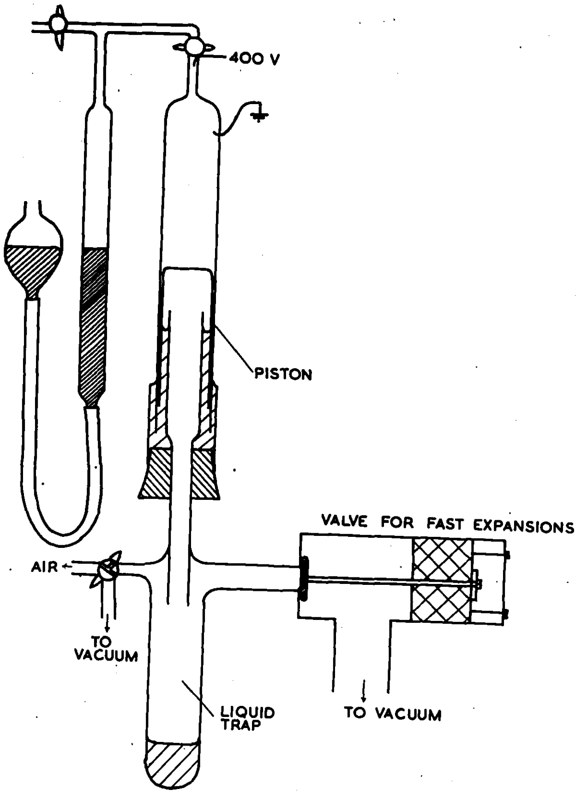


Figure 6. Diagram of small expansion chamber.

as the ratio could be preset to any required value. A potential of 400 V could be applied across the chamber. The chamber was illuminated with a steady lamp and observed visually.

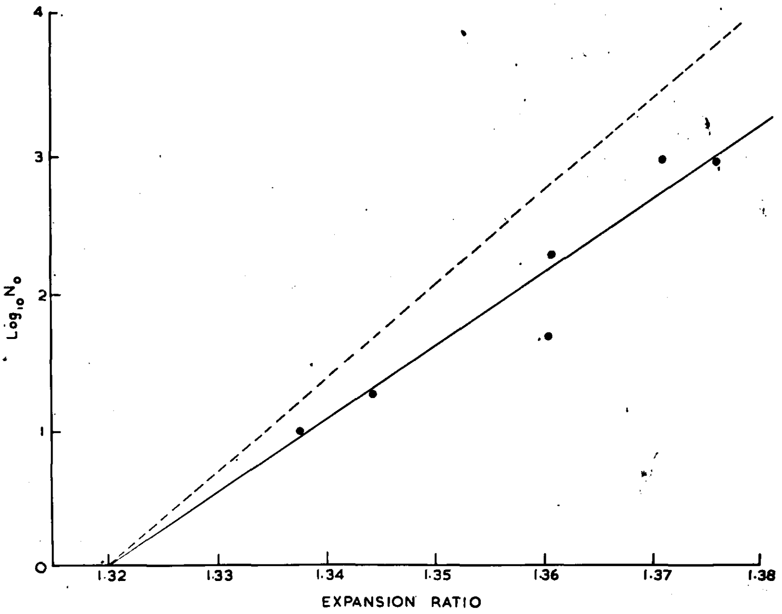
Procedure

For the condensation experiments, the drop density after each expansion was simply estimated visually. This could be done fairly accurately, perhaps to within a factor of 3. This method was found to be sufficiently accurate for the present purpose.

Since the chamber was quite small ($V/A = 0.5$ cm), the gas in the chamber would reach temperature equilibrium fairly quickly. All the fast expansions were therefore made with a delay of 30 seconds after the last compression.

Results for Water

The results for water are shown in Figure 7. The increase in drop density predicted by Equations (1) and (2), is also shown in the same figure, the constants



<u>Figure 7.</u> Variation of drop density with expansion ratio, for water (initial temperature 20.0°C). Full line, observations in small chamber; broken line, calculated variation.

F and t_e again being adjusted so as to give agreement at a drop density of $1/cm^3$. It will be seen that, within the error involved in the rough estimate of the drop density, the increase in the drop density with expansion ratio is in approximate agreement with that observed in the large chamber.

The drop density reached a value of $1/cm^3$ at an expansion ratio of 1.32 ± 0.01, corresponding to a supersaturation of 5.9 ± 0.3, and a final nominal temperature of 262.2°K. The increase in the expansion ratio and the supersaturation is to be expected from the effectively shorter duration of the supersaturation in the smaller chamber. The effective time, t_e, is estimated to be of the order of 10^{-4} seconds for this chamber. For the above supersaturation, the Becker & Döring formula predicts a rate of drop formation of $10^{5.3}$, and thus a drop density of about $20/cm^3$.

It therefore appears, that the results with the small cloud chamber, do not differ significantly from that found with large cloud chambers.

Observations with Alcohols

The study was also extended to ethyl and methyl alcohol, both of which are very interesting liquids from the point of view of condensation. Both samples of alcohols were carefully dried by reflux condensing over calcium oxide for several hours and then distilling over in a dry atmosphere.

The results for ethyl alcohol is shown in Fig. 8. The figure also shows the increase in the number of drops calculated from Equations (1) and (2), again normalised at a drop density of $1/cm^3$. This drop density occurred at an expansion ratio of 1.20 ± 0.01, corresponding to a supersaturation of 2.5 ± 0.2 and a final temperature of $274.6^{\circ}K$. This supersaturation is in satisfactory agreement with the value of 2.30 at $273^{\circ}K$, observed by Volmer & Flood in a large chamber.

The results for methyl alcohol is shown in Figure 9. In this case the drop density of $1/cm^3$ corresponded to an expansion ratio of 1.35 ± 0.01, a supersaturation of 4.0 ± 0.2 and a final temperature of $263.3^{\circ}K$. The supersaturation is again in good agreement with the value of 3.20 at $270^{\circ}K$, observed

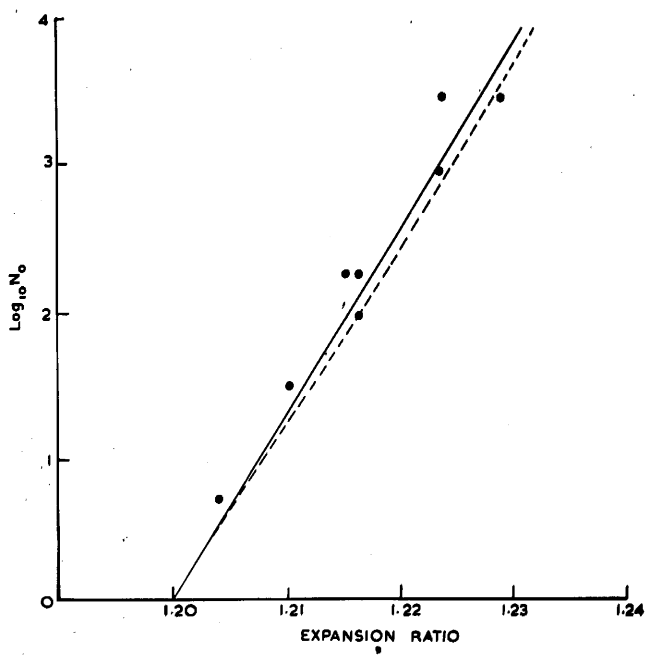


Figure 8. Variation of drop density with expansion ratio, for ethyl alcohol (initial temperature 20.0°C). Full line, observations in small chamber; broken line, calculated variation.

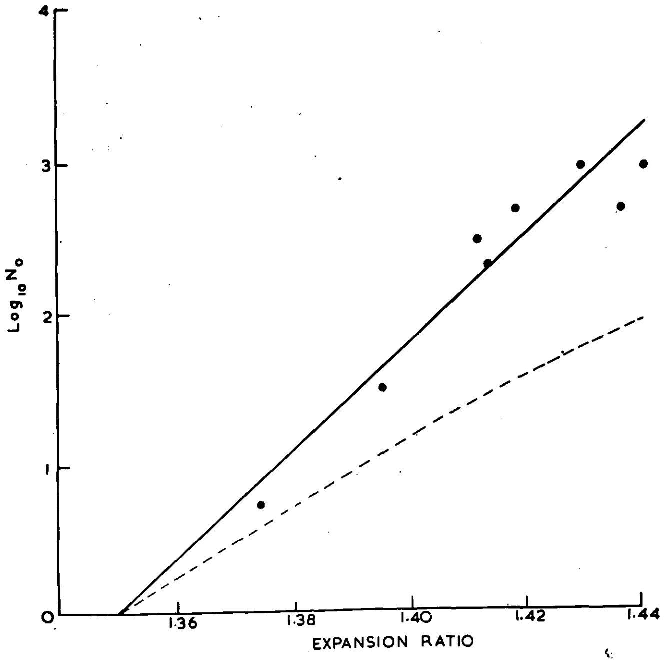


Figure 9. Variation of drop density with expansion ratio, for methyl alcohol (initial temperature 20.0°C). Full line, observations in small chamber; broken line, calculated variation.

by Volmer & Flood in a large chamber. The number of drops expected from the Becker & Döring formula at the observed supersaturation is 10^{16}, which is thus much in excess of the observed value. It will be seen from Figure 9 that the increase in drop density with expansion ratio is much in excess of the rate predicted by the theory.

Conclusion

The results obtained with the small cloud chamber, were therefore found to be in good agreement with those in larger chambers, when the effective duration of the supersaturation was taken into account. This conclusion shows that under normal conditions, there are not a significant number of nuclei produced by contaminations in large chambers

DISCUSSION

The above experiments clearly indicate the need for careful specification of the corresponding condensation rate when referring to a certain 'critical supersaturation' or 'limit'. If this is done, then the apparently different results obtained by previous workers can be understood. The experiments indicated, for instance, that the 'critical supersaturation' of Volmer & Flood and Scharrer probably corresponded to a final drop density of $1/cm^3$, rather than a condensation rate of 1 drop/cm^3second.

The marked disagreement between the theory and experiment for methyl alcohol may again be stressed. It seems possible that the explanation of the discrepancy may be that the properties of the small complexes of methyl alcohol are rather different from that of ethyl alcohol, for instance. In this connection it may also be noted that for some of the liquids studied by Scharrer there is also a large discrepancy. Thus for instance, Scharrer measured the 'critical supersaturation' for benzene to be 5.3 at 251^oK, and for carbon tetrachloride to be 6.5 at 247^oK. In both cases, the supersaturation calculated from the Becker & Döring formula, corresponding to a condensation rate even as low as $1/cm^3$second, was found to be 9.3. There is thus again a marked disagreement for these liquids.

For a more complete indication of the extent of the validity of the theory, it would be very useful to have measurements on as wide a variety of liquids as possible. The best technique for this purpose seems to be one in which the drop density is determined as a function of the expansion ratio. For such a photographic technique, it would be desirable to arrange the area of photography so that the drop density can be studied in range of 10 to 10^4 per cm^3. The lower limit is set by the inevitable occurrence of some stray drops, which for instance had not been cleared by the slow expansions. Again, at drop densities above $10^4/cm^3$, the heat of condensation of the drops will start to affect the subsequent condensation, making the interpretation difficult.

PART III

A STUDY OF THE CONDENSATION NUCLEI PRODUCED BY ULTRA-VIOLET LIGHT

INTRODUCTION

It was discovered by Lenard & Wolff (1889) that when moist dust free air was exposed to ultra-violet light and then expanded, it gave rise to a dense cloud. This showed that the ultra-violet light produced some kind of condensation nuclei in the gas, even though the light was not of sufficiently short wave-length to cause ionization. These uncharged condensation nuclei were studied subsequently by Wilson (1899) and more recently by Crane & Halpern (1939), Farley (1951) and McHenry & Twomey (1952).

A critical review of the previous experimental work will be given in the next section, where it will be pointed out that the results to date do not permit a detailed explanation of the effect. In particular, the component of the gas which on radiation, gives rise to the nuclei, has not been conclusively identified. A more thorough study of these condensation nuclei was therefore undertaken. The results of the investigation are described in the later sections.

REVIEW OF PREVIOUS EXPERIMENTAL WORK

Experiments of Wilson

C.T.R. Wilson (1899) made an extensive study of the condensation of water vapour on nuclei produced on admitting ultra-violet light through a quartz window into a cloud chamber. He showed that the nuclei were formed throughout the illuminated volume, and they could therefore not be small particles arising from the disintegration of the quartz window, as had been suggested by Lenard & Wolff.

Wilson also studied the minimum expansion which would produce a cloudlike condensation in the chamber immediately after illumination with ultra-violet light. With the relatively weak light intensity obtained by using a zinc spark as source, a volume expansion of the order of 1.25 was found to give rise to a cloud. The expansion required could be reduced by increasing the exposure time, up to a certain point when no further decrease could be observed. When a delay was introduced between the exposure and the expansion, the density of the cloud decreased rapidly, and after 30 seconds very little condensation could be observed.

The minimum expansion required for cloud formation could be reduced by increasing the intensity of the ultra-violet light. In fact, Wilson found that in air saturated with water vapour, an intense beam from a carbon arc produced nuclei which required only small expansions to produce a cloud. With this intense light, clouds were also produced in oxygen and carbon dioxide on small expansions, but in hydrogen a relatively large expansion was required for condensation.

Wilson suggested that the clouds were due to the formation of hydrogen peroxide by the action of the light on the water and oxygen. A small drop containing some hydrogen peroxide would then grow more easily by virtue of the lowering of the equilibrium vapour pressure by the dissolved substance. It is clear that this explanation does not account for the formation of the clouds in carbon dioxide and hydrogen.

Observations of Crane & Halpern

Crane & Halpern (1939) observed that ethyl alcohol also condensed readily on the nuclei formed by the action of ultra-violet light. They admitted light from a small arc through a quartz window into an expansion chamber filled with air saturated with ethyl alcohol. On expansion, a dense cloud was produced in the path of the beam. A clearing field had no effect on the cloud, so they were satisfied that the condensation did not take place on ions. They ascribed the formation of the cloud to the liberation of atomic oxygen in the chamber by the light, but gave no evidence to justify this assumption.

Experiments of Farley

Farley (1951) recently investigated the condensation of water vapour on ultra-violet light nuclei. For these experiments he used a conventional cloud chamber of the rubber diaphragm type, with a quartz window for admitting a narrow beam of ultra-violet light from a high-pressure mercury discharge lamp. In the first series of experiments, the chamber was filled with air saturated with water vapour.

On exposing the chamber to the light for 0.1 seconds, and expanding immediately afterwards, a dense cloud was observed at an expansion ratio of about 1.30, the cloud being approximately confined to the narrow illuminated region. If a delay was introduced between the exposure and the expansion, the cloud was observed to spread, due to the diffusion of the nuclei before causing condensation. By measuring the width of the cloud produced at different intervals after the exposure, Farley estimated that the diffusion coefficient of the nuclei was at least as great as that of ions. This showed conclusively that the nuclei were uncharged, as they were not removed by the electric clearing field.

Farley also studied the effect of passing the ultra-violet light through various filters. With a filter of glacial acetic acid, absorbing light of wavelength below 2400 A.U., a dense cloud could still be observed. Only a faint cloud was produced when carbon tetrachloride used to absorb wavelengths below 2530 A.U. No cloud could be observed when a piece of pyrex glass was introduced in the beam.

From these observations, Farley estimated the wavelength of the light responsible for the effect to be in the region 2400 to 2530 A.U. Now Herzberg (1932) has shown that oxygen absorbs weakly in this region, corresponding to dissociation into two uncharged atoms. Farley therefore suggested that the primary step in the formation of the nuclei is the liberation of atomic oxygen.

This conclusion was tested by filling the chamber with argon from which the residual oxygen had been removed by passing over heated copper. After irradiating with ultra-violet light and expanding, only a very faint cloud was observed in the path of the beam. This was attributed to oxygen coming from the rubber diaphragm.

The evidence given by Farley does not prove conclusively, however, that the effect is indeed due to the dissociation of oxygen. It must be remembered that experiments with light over a varying spectral range are difficult to interpret unless a sudden change in the drop density can be observed. Although the appearance of the cloud may change appreciably when a small region of the spectrum is eliminated, it is possible that the drop density changes gradually with wavelength. In this case the limit at which the condensation becomes noticeable will of course depend on the light intensity. As Farley only observed the density of the cloud visually, his estimate of the critical wavelength may only be approximate. Furthermore, the faint cloud obtained with purified argon is difficult to explain on the assumption that the effect is due to oxygen. It seems unlikely that enough oxygen would be given off by the rubber diaphragm to cause noticeable condensation.

Experiments of McHenry & Twomey

To study the condensation nuclei produced by ultra-violet light, McHenry & Twomey (1952) used a form of cloud chamber called a Nolan-Pollak dust counter. In this chamber the drop density after expansion was estimated from the diminished intensity of the beam of ultra-violet light passing through the cloud, as measured by a photocell at the end of the chamber. The observations were all done at a fixed expansion ratio of 1.18.

McHenry & Twomey also attempted to determine the maximum wavelength of the light which would just produce nuclei, again by using filters to limit the spectral region used. They found that the beam caused no condensation after passing through a filter which transmitted wavelengths down to 2400 A.U. Some condensation was observed when the beam passed through a filter which transmitted down to 2345 A.U. The critical wavelength for nucleus formation was therefore considered to be between 2345 and 2400 A.U. This corresponds to the region where ammonia starts to absorb. McHenry & Twomey also found that the addition of small quantities of ammonia to the chamber resulted in a great increase in the number of drops. They therefore suggested that the production of nuclei in air by ultra-violet light is due to the presence of ammonia as impurity.

With nitrogen as the permanent gas in the chamber, they observed after radiation approximately twice as many drops as with air. On the other hand, very few drops were observed with oxygen.

The experiments of McHenry & Twomey are, however, open to severe criticism. As they did not vary the expansion ratio, their results are incomplete and thus difficult to interpret. Their suggestion that the nuclei are formed as a result of the presence of ammonia as contamination, needs to be verified. It has been pointed out that it is difficult to draw any definite conclusions from work with different parts of the spectrum, unless a sudden increase in the drop density can be observed. It furthermore seems unlikely that there is enough ammonia present in the atmosphere to account for the dense clouds observed with air and water vapour.

Conclusions

It has thus been observed by a number of workers that even relatively weak ultra-violet light produces nuclei on which drops are formed at supersaturations comparable to that required for condensation on ions. It has definitely been shown, however, that the nuclei are uncharged, but otherwise very little is known about them.

EXPERIMENTS WITH LARGE CLOUD CHAMBER

In the experiments described in this and the next section, the properties of the ultra-violet light nuclei were systematically investigated. The object of these investigations was to attempt to determine the nature of the nuclei, and thus give an explanation of the effect. The first series of experiments was done in a large cloud chamber of conventional design.

Apparatus

A diagram of the apparatus is shown in Figure 1. The cloud chamber was of the rubber diaphragm type, and was 9 inches in diameter and 2 inches high. A black velvet cloth wetted with the liquid in use, served as the vapour source and background for photography. A potential of 400 V could be applied to the lead wire gasket between the top glass plate and the glass cylinder. An alpha-source fixed to the inside of the cylinder served as a convenient reference.

The cylinder had a quartz window for admitting the beam of light from a high pressure mercury

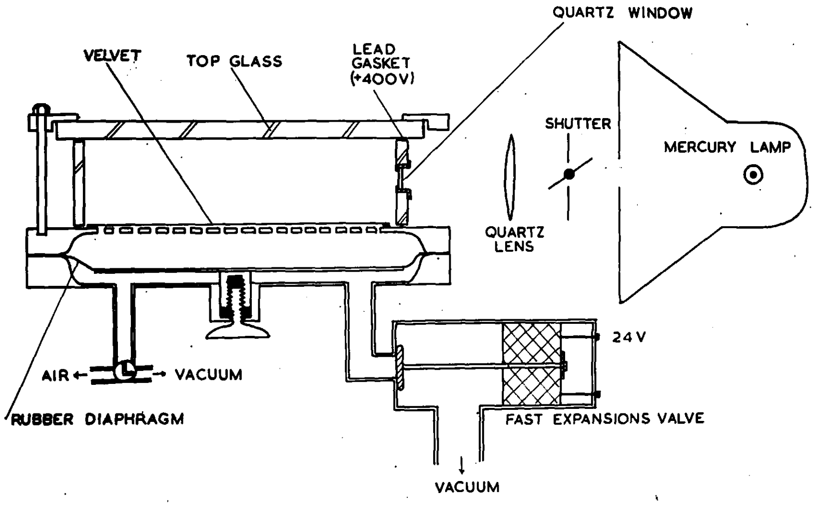


Figure 1. Diagram of arrangement for ultra-violet light experiments in large expansion chamber.

discharge lamp. The beam was defined by two stops, and the light brought to a focus inside the chamber with a quartz lens. The duration of the exposure could be controlled with a shutter.

The chamber was normally illuminated with a horizontal beam of light from a steady lamp and observed visually. If desired, however, it could also be illuminated with two flash tubes, and photographed with a 60 mm camera.

Procedure for Observations

Figure 2 shows the effect produced on exposing the chamber (containing air saturated with water vapour) to a narrow beam of ultra-violet light and expanding immediately afterwards. An expansion ratio of 1.30 was used, and the clearing field continuously maintained, so that few drops formed outside the illuminated region. It will be seen that the ultra-violet light produced a dense cloud, approximately confined to the narrow beam.

On increasing the duration of the exposure, the cloud became denser, and its width also increased as

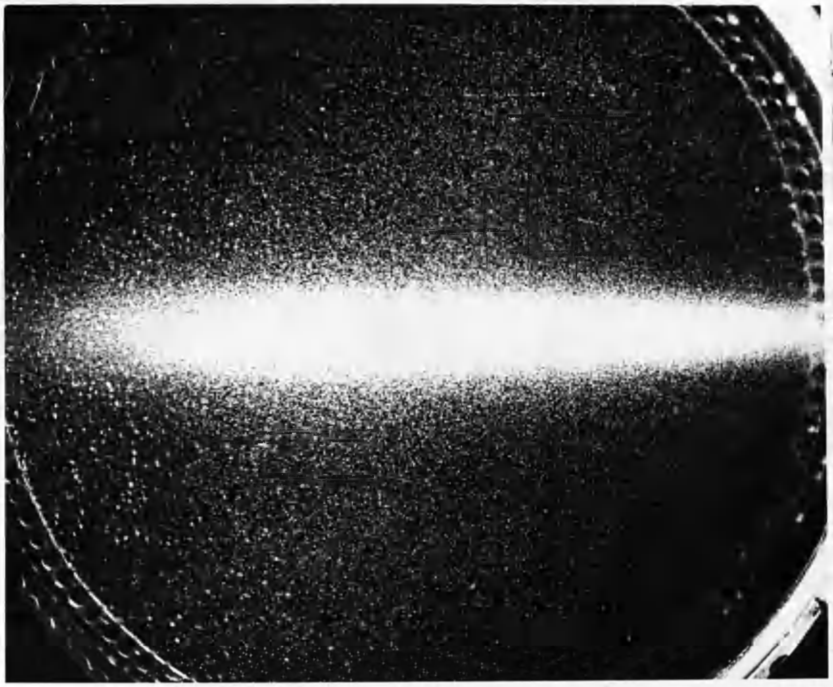


Figure 2. Cloud produced by ultra-violet beam; exposure 0.5 seconds, expansion ratio 1.30.

a result of the diffusion of the nuclei before condensation. The cloud density did not increase indefinitely with exposure time, but attained a sensibly constant value after about 30 seconds. Apparently, after radiating for this time, the density of the nuclei reached equilibrium, the number of nuclei formed then just balancing the number removed by diffusion and perhaps recombination.

The number of drops decreased rapidly when a delay was introduced between the exposure and the expansion. If the expansion was made about one minute after the exposure, then no increased condensation could be noticed in the region that had been illuminated.

On decreasing the expansion ratio, the density of the cloud decreased rapidly, and finally no condensation could be observed, even with continuous radiation. It was therefore possible to observe a 'critical expansion ratio for ultra-violet condensation'. For the present investigation this is defined as the expansion ratio at which the condensation in the cloud chamber just becomes noticeable after radiating for long enough for the equilibrium density of nuclei to be set up. It must be pointed out that this definition is only arbitrary, as the ratio will of course depend on the light intensity and the amount of condensation that can just be distinguished. Nevertheless, the 'critical ratio' was found to be a very useful criterion for making comparisons of the effect under different conditions.

It is to be expected that this 'critical ratio' will depend on the temperature and vapour pressure conditions in the chamber. This variation can be conveniently taken into account by comparing the above ratio with the 'critical ratio for ion condensation'. This is defined for the present as the expansion ratio at which the condensation round the alpha-source can just be distinguished, after the field has been left off for for long enough for the equilibrium ion density to be reached. This arbitrary ratio again proved to be very useful in making comparisons. Both critical expansion ratios were found to be relatively sharply defined, so that they could be estimated quite accurately.

It was noticed by Farley (1951) that the density of the ultra-violet cloud depended on the interval between the expansion and the preceding compression.

A similar variation in the density of the cloud was noticed here. The variation in the cloud density is of course due to the variation in the temperature and vapour pressure in the chamber as a result of the compression. To eliminate errors due to this effect, the expansions in a series of experiments were always made at a fixed interval after the final compression. An interval of 30 seconds was normally used, as this allowed ample time for the equilibrium distributions of the ions and the ultra-violet light nuclei to be set up.

Diffusion Coefficient of the Nuclei

The experiment done by Farley (1951) to measure the diffusion coefficient of the ultra-violet light nuclei, was repeated.

The chamber was exposed to a narrow beam of light for 0.2 seconds and expansions made after varying delays. The chamber was illuminated with the flash lamps and the clouds photographed. By replacing the film back in the camera after developing, and reprojecting on to a screen, the apparent width of the beam could be estimated for each delay. Fig. 3 shows

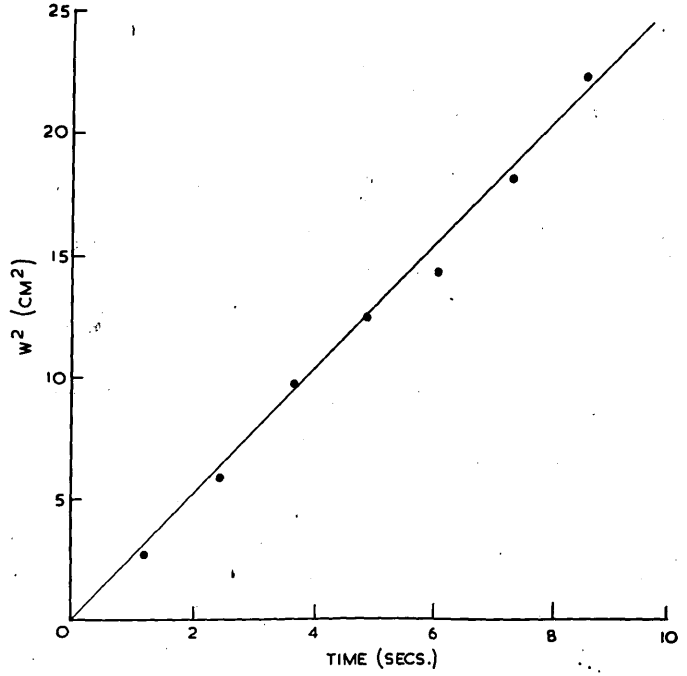


Figure 3. Variation of the width, w, of the ultraviolet cloud with delay time.

the observed variation in the width of the beam with delay time.

Farley interpreted his results by using the theory developed by Jaffe (1913) and Blackett (1934) for the diffusion of a column of ions. In the form used by Farley it is assumed implicitly, however, that each drop is formed on a single nucleus. Since this is not necessarily the case, the theory must be modified correspondingly as follows.

Suppose for simplicity that the nuclei are formed instantaneously in a narrow column, containing Z_o' nuclei per cm. Then the density of the nuclei at a distance ξ from the initial column after a time t will be given by the equation derived by Jaffe,

$$Z' = \frac{Z_o'}{4\,D't} \,\mathrm{Exp}\,(-\xi^2/4D't) \quad , \qquad (1)$$

where D' is the diffusion coefficient of the nuclei, and the effect of recombination has been neglected.

If on the average ν nuclei are required for the formation of a single drop, then the drop density N' can be taken to be approximately proportional to $(Z')^\nu$. Therefore the drop density at a distance ξ from the centre of the beam will be given by

$$N' = N_o' \operatorname{Exp}(-\nu\zeta^2/4D't) \quad , \qquad (2)$$

where N_o' is a factor independent of ζ. Following Blackett, the 'width' of the cloud may conveniently be taken to be that which in a projection contains 90% of the drops. By integrating (2), this will therefore be given by

$$w = 4.68(D't/\nu)^{\frac{1}{2}} \quad , \qquad (3)$$

so that Blackett's equation as used by Farley is simply modified by replacing D' by D'/ν.

The effect of recombination, which has been neglected so far, may be important for the ultraviolet light nuclei. Jaffe has shown, however, that the effect of recombination approximately just reduces the term Z_o' in (1), while the distribution of the nuclei is kept unaltered. Hence the 'width' of the cloud will not be affected by recombination.

On comparing the results in Figure 3 with Equation (3), and reducing the diffusion coefficient to N.T.P., assuming it to be inversely proportional to the pressure and proportional to the square of the temperature, it was found that

$$D'/\nu = 0.09 \text{ cm}^2/\text{sec}. \qquad (4)$$

This value is in good agreement with Farley's estimate for D'. As pointed out by Farley, this estimate is only of limited accuracy, since the theoretical definition of the 'width' may not be entirely consistent with the apparent width measured.

Nevertheless, it can be concluded that whatever the value of ν, D' will be greater than the diffusion coefficient of ions, which is of the order of 0.03 cm^2/second in air at N.T.P. Thus Farley's conclusion that the nuclei are uncharged since they are not removed by the electric field, is still valid.

Another important conclusion which can be drawn from the relatively large value of D'/ν, is that the drops are in fact probably formed on single nuclei. The value of D'/ν may be compared with the diffusion coefficients of some other substances in air at N.T.P., for example 0.24 cm^2/second for water vapour and 0.18 cm^2/ second for oxygen. As the nuclei cause condensation, it can be expected that they will have some water molecules attached to them. The diffusion coefficient of the resulting complex will thus be small compared to that of water vapour. Hence it follows that ν must be small, and is in fact most probably equal to unity.

Experiments with Alcohols

Crane & Halpern (1939) observed that ultra-violet light also promoted the condensation of ethyl alcohol. A series of experiments was made to investigate the condensation of ethyl and methyl alcohol after irradiation with ultra-violet light.

With air in the chamber saturated with either ethyl or methyl alcohol, the condensation phenomena were observed to be very similar to that with water. In Table 1 the critical expansion ratios for these liquids are compared with that for water (using approximately the same light intensity).

Table 1. Critical Expansion Ratios for Air with Different Liquids

Liquid	Critical Expansion Ratios		
	U.V.	Ion	Diff.
Water	1.243	1.272	0.029
Ethyl Alcohol	1.174	1.186	0.012
Methyl Alcohol	1.182	1.196	0.014

It will be seen that the expansion ratios for ultra-violet condensation are consistently lower than that for ion condensation. This suggests that the nuclei in the three cases are similar, and are therefore not primarily due to reaction products of the vapours. Further evidence for the above conclusion was obtained from experiments with water and ethyl alcohol using light from different regions of the spectrum. In these experiments various absorbers were placed in the path of the beam and the modified critical expansion ratios determined. The results are shown in Table 2.

Table 2. Effect of Absorbers on the Critical Expansion Ratios.

Absorber	Critical Expansion Ratios	
	Ethyl Alcohol	Water
No	1.186	1.243
Water	1.200	1.263
Absolute alcohol	1.220	1.295
Carbon tetrachloride	1.230	1.315

Some condensation was still observed both with water and ethyl alcohol even after the radiation had passed through a filter of carbon tetrachloride, which removed light of wavelengths below about 2530 A.U. Now water vapour, for instance, only starts to absorb strongly at wavelengths below 2000 A.U. (Rollefson & Burton, 1939). It therefore seems unlikely that the nuclei arise from the dissociation or excitation of the vapour by the radiation. Moreover, the condensation of water and ethyl alcohol was found to be similarly affected by light of different wavelengths, which again would not be expected if the nuclei were due to light absorption by the vapour.

Experiments with Different Permanent Gases

The above experiments indicated that the nuclei did not arise from the vapour, and therefore must have been formed in the air. To investigate which component of the air was responsible for the production of the nuclei, the effect was studied with different permanent gases in the chamber. In particular, the condensation in oxygen-free gases was investigated, to check whether the nuclei arose from the dissociation of oxygen, as suggested by Farley.

The condensation in different gases was conveniently compared by means of the critical expansion ratios for ions and ultra-violet light nuclei, using the same light intensity throughout. Table 3 shows the observed critical expansion ratios for water vapour, for relatively weak light intensity.

With cylinder nitrogen and oxygen in the chamber respectively, the expansion ratios did not differ significantly from that in air. With argon, the difference between the critical expansion ratios was found to be smaller than with the diatomic gases, as would be expected from its larger ratio of specific heats.

Since no difference could be observed between cylinder oxygen and cylinder nitrogen (which contained less than 1% oxygen impurity) it seemed rather unlikely that the ultra-violet effect could be due to the dissociation of oxygen. This conclusion was checked carefully by repeating the experiment with gases from which the oxygen had been removed. For these experiments, some freshly boiled distilled water was put into the chamber. The chamber was then filled with

Table 3. Critical Expansion Ratios for Water With Different Permanent Gases

Gas	Critical Expansion Ratios		
	U.V.	Ion	Diff.
Air	1.311	1.276	0.035
Cylinder oxygen	1.309	1.274	0.035
Cylinder nitrogen	1.306	1.274	0.032
Cylinder argon	1.183	1.160	0.023
Pure nitrogen	1.298	1.268	0.030
Pure argon	1.185	1.161	0.024
Pure hydrogen	1.295	1.265	0.030

gases which had been passed over a copper gauze contained in a quartz tube heated to 700°C. The purification process had practically no effect on the critical expansion ratios in nitrogen and argon. The experiment was also done with hydrogen which had been passed over heated copper, and the critical ratios observed to be approximately the same as for the other diatomic gases. In hydrogen, however, the cloud was observed to be noticeably thinner than with these gases. This is understandable, since the nuclei will have a fairly large diffusion coefficient in hydrogen. Since most of the nuclei are probably removed by diffusion, the equilibrium density of the nuclei will be correspondingly less in hydrogen.

The above results show clearly that the formation of the nuclei does not depend on the permanent gas in the chamber. Contrary to the observations of Farley, a dense cloud was obtained in argon from which the oxygen had been removed. In fact, in the course of the experiments with oxygen and purified nitrogen, the oxygen concentration was reduced by a factor of at least a thousand, without any appreciable effect on the critical expansion ratio. It can therefore be concluded that the nuclei are not formed as a result of the dissociation of oxygen.

During the course of these experiments an effect was noticed which could explain Farley's observation with argon, and which also indicated the source of the nuclei. It was namely noticed that the critical expansion ratio decreased appreciably with the period the permanent gas had been confined the the cloud chamber. This corresponds to an increase in the density of the cloud with time, indicating a gradual increase in the number of nuclei.

With the weak source used for the above experiments, the effect was rather difficult to observe, and was overlooked at first. The most marked increase took place during the initial stages when the gas had just been put into the chamber. During this time the gas had not yet been cleaned from all the contaminating nuclei, so that observations were rather difficult.

To eliminate the effect in the measurements comparing the expansion ratios in different gases, the above experiments were therefore all made after the gas had been in the chamber overnight.

Increase in Number of Nuclei with Time

The gradual increase in the number of nuclei with the period the gas had been in the chamber, indicated that the nuclei were due to some substance produced in the chamber. A careful study was made of this effect, again by means of the variation in the critical expansion ratios.

For this investigation, a quartz lens was used to produce a more intense beam of light in the chamber.

The first series of experiments was done with distilled water as condensant. Table 4 shows the variation in critical expansion ratio with nitrogen as the permanent gas.

Table 4. Variation in Critical Expansion Ratio with Time, for Nitrogen-Water Vapour

Time (hrs.)	Critical Expansion Ratios	
	U.V.	Ion
0.2	1.282	1.272
4.0	1.243	1.272
18.0	1.228	1.273

It will be seen that there is a significant decrease in the limit for ultra-violet condensation, while the ion limit stays effectively constant. Similar results were also obtained with oxygen in the chamber. For oxygen, the ultra-violet critical ratio was found to decrease from 1.277 to 1.245 in two days, while the ion limit stayed constant approximately.

An experiment was also done to check that the effect was not enhanced by expansions and radiations. Fresh oxygen was put into the chamber, and left for two days, without any expansions or radiation. It was then found that the ultra-violet critical ratio was 1.240, while the ion limit was practically the same as before. Therefore the effect merely depends on the time the gas had been in the chamber.

The experiments were repeated using ethyl alcohol as condensant. The variation of the critical expansion ratio with time for a nitrogen filling, is shown in Table 5. A marked decrease in the critical expansion ratio for ultra-violet light condensation, was again observed. Similar results were also obtained with oxygen and with air in the chamber.

Thus using either water vapour or ethyl alcohol as the condensant, the critical expansion ratio for ultra-violet condensation decreased markedly with time. In conclusion it may be remarked that this effect may be the reason why Farley observed such a faint cloud in purified argon. If he made the observation shortly after the argon had been put into the chamber, then the condensation would have been very much reduced as compared to that in air (which presumably had been in the chamber for a considerable period).

Table 5. Variation in Critical Expansion Ratios with Time, for Nitrogen-Ethyl Alcohol

Time (hrs.)	Critical Expansion Ratios	
	Ion	U.V.
1.5	1.267	1.295
5.0	1.248	1.246
18.5	1.243	1.231
29.0	1.245	1.222
44.5	1.249	1.220
92.5	1.243	1.212

Conclusion

The experiments with a large expansion chamber have indicated some of the properties of the nuclei formed as a result of ultra-violet light radiation. It has been found that single nuclei are probably sufficient for the production of drops. The formation of the nuclei is independent of the permanent gas, and the nuclei produce condensation of different vapours. The seem to arise from some gas or vapour which is continuously being produced in the chamber.

The chamber gas comes mainly into contact with brass, glass, the rubber of the diaphragm and the velvet serving as vapour source. Of these materials, the rubber seems to be the most likely source of a gaseous emanation. As a first step in the identification of the contamination, the material producing it should be isolated.

For this purpose it would be convenient to have a chamber in which the contamination has been eliminated. Experiments were therefore done with a small cloud chamber, in which only glass and the condensant came into direct contact with the expanding volume. The experiments with this chamber are described in the following section.

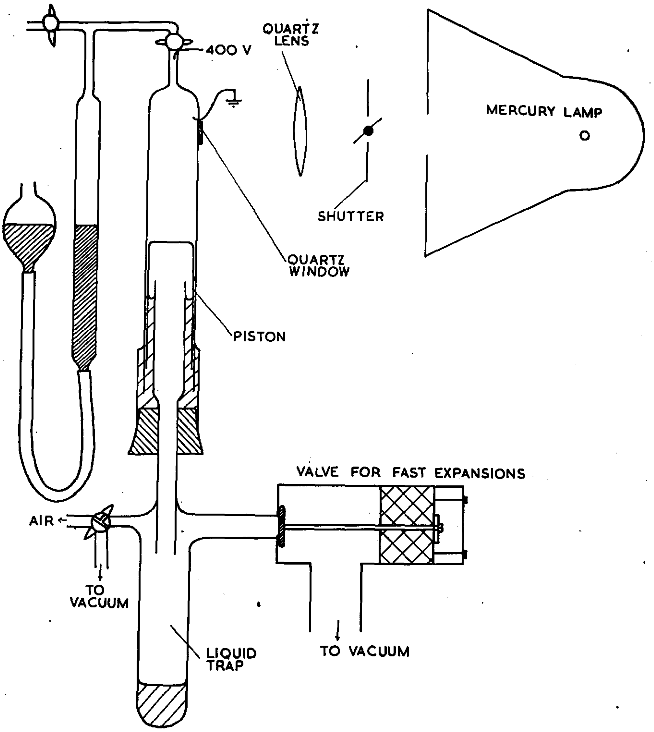
EXPERIMENTS WITH SMALL CLOUD CHAMBER

The results of the previous section indicated the desirability of studying the effect in a cloud chamber less likely to give rise to contaminations.

A cloud chamber was therefore constructed of essentially the same design as used by Wilson in his original investigation. This cloud chamber could be cleaned quite readily. Moreover, it was of some interest to repeat Wilson's experiments in a cloud chamber of similar design.

Apparatus

A diagram of the apparatus is shown in Figure 4. The cloud chamber consisted of a glass tube sealed off at the top by a capillary tube and tap. The other end was closed by a rubber stopper. The working volume of the chamber was sealed off by a glass piston floating in the liquid in use, the ends of the piston being ground flat. To expand the chamber volume, the space underneath the piston was suddenly connected to a vacuum, so that the piston moved rapidly downward and came to rest on the rubber stopper. The expansion ratio was adjusted by changing the volume of gas above the piston by means of the manometer. The expansion ratio was simply estimated from the displacement of the piston, the effective length of the chamber in the expanded position being 9.73 cms.



<u>Figure 4.</u> Arrangement used for ultra-violet experiments with small cloud chamber.

The chamber had a quartz window near the top, fixed to the glass with Apiezon Wax W40. The light from a high pressure mercury discharge lamp could be brought to a focus inside the chamber with a quartz lens, after passing through two stops and a shutter. The chamber was illuminated with a steady lamp and observed visually. A potential of 400 V could be applied between two electrodes in the chamber; the chamber was usually operated with the field continuously maintained.

Method of Observation

Most of the observations were made by simply estimating the drop density visually after an expansion. This could be done fairly accurately, perhaps to within a factor of 3, which was sufficiently accurate for the purpose of most of the following experiments. The experiments usually involved a comparison of the drop densities with and without the radiation, which could be done with greater accuracy than the estimate of the absolute drop density.

The temperature and vapour pressure inside the small chamber came to equilibrium very quickly after an expansion or compression, very little change taking place after 30 seconds. The expansions were usually made with a delay of 30 seconds after the last compression, which also allowed ample time for the density of ultra-violet nuclei to reach equilibrium.

Preliminary Results with Water

The first series of experiments with the small chamber was made with air and distilled water. The results of a typical series of expansions at different ratios, alternatively with and without exposure to ultra-violet light, are shown in Fig. 5, in which the logarithm of the drop density is plotted as a function of the expansion ratio.

The logarithm of the background drop density can be seen to increase approximately linearly with expansion ratio. The drop density after exposure to ultra-violet light at first increases very rapidly with expansion ratio, but at large ratios the number of drops formed is not much different from that in the absence of radiation.

Figure 6 shows the logarithm of the density of drops formed on the ultra-violet light nuclei only,

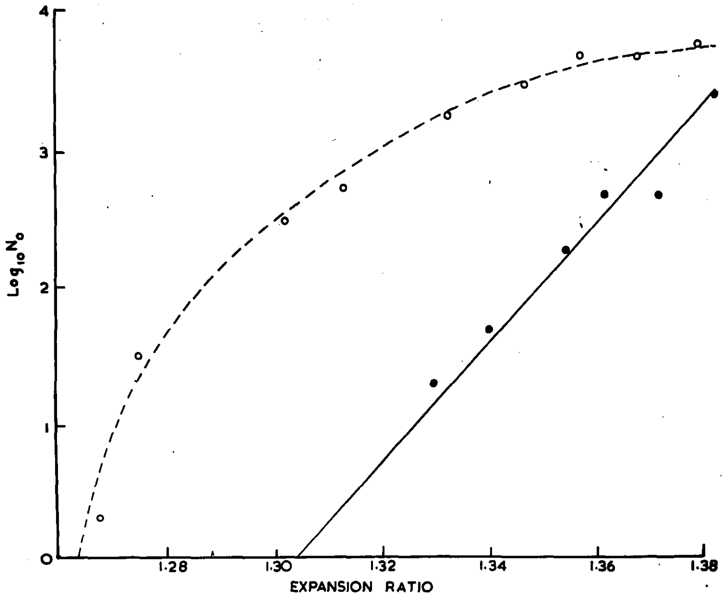


Figure 5. Variation of drop density, N_o, with expansion ratio with ultra-violet radiation (dotted curve) and without radiation (full curve).

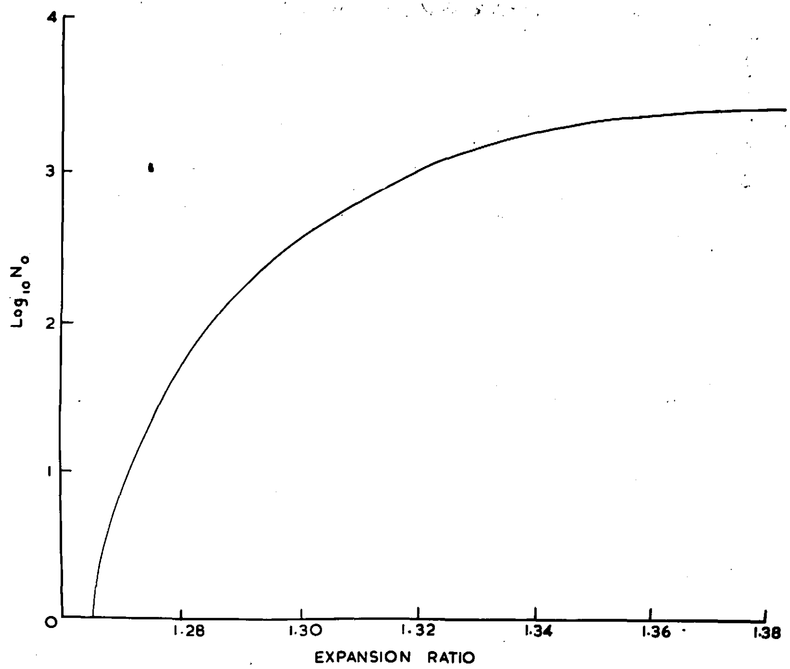


Figure 6. Variation of the number of drops formed on nuclei as a function of expansion ratio (water vapour and air).

calculated from the data in Figure 5. It will be seen that at large expansion ratios a stage is reached when the number of drops shows practically no increase with expansion ratio. The limiting drop density was estimated to be of the order of a few thousand per cm^3. It thus appears that at the large expansion ratios a stage is reached when all the nuclei cause condensation.

Although the method of estimating the drop density was only very approximate, there can be little doubt that the number of drops reached a limiting value at large ratios. If the number of drops formed on the nuclei increased at the same rate as the background, for instance, then a dense cloud should be seen at an expansion ratio of 1.33, whereas in fact separate drops could still be distinguished. It may perhaps be pointed out that the limiting drop density is too small for the heat of condensation to have the effect of limiting the drop density.

The density of the ultra-violet cloud was much smaller than observed in the large chamber with approximately the same light intensity. Hence most of the contamination which gave rise to nuclei in the large chamber, had been eliminated. On passing fresh air into the chamber and the manometer reservoir, a slight decrease in the density of the nuclei was observed (after the chamber had been cleaned of dust by slow expansions). With nitrogen in the chamber, the density of the ultra-violet light nuclei was again estimated to be of the order of a few thousand per cm^3.

The variation in the number of nuclei formed by light of varying intensity, was also studied. The light intensity was varied by adjusting the aperture of the shutter, and for each aperture the number of nuclei estimated by the method illustrated in Fig. 6. From Table 6 it will be seen that the equilibrium

Table 6. Variation in Number of Nuclei with Light Intensity

Aperture	Nuclei/cm^3
1	3000
4	1000
16	500

number of nuclei increased with the light intensity. The estimate of the density of the nuclei was not sufficiently accurate, however, to be able to determine whether the number increased linearly with the light intensity.

Experiments with Alcohols

Figure 7 shows the results of a series of expansions at different ratios, alternately with and without ultra-violet radiation, in a chamber containing air and absolute alcohol. No difference in the drop density could be observed, whether the chamber had been exposed to the light or not. Thus the chamber in this case contained a neglible amount of substance giving rise to nuclei on radiation. Exactly the same result was obtained with methyl alcohol; again the radiation had no appreciable effect on the drop density.

The experiments were repeated with mixtures of water and ethyl alcohol. For each mixture the total number of nuclei were estimated by the method illustrated in Figure 6. The densities of the nuclei for the different mixtures, are shown in Table 7.

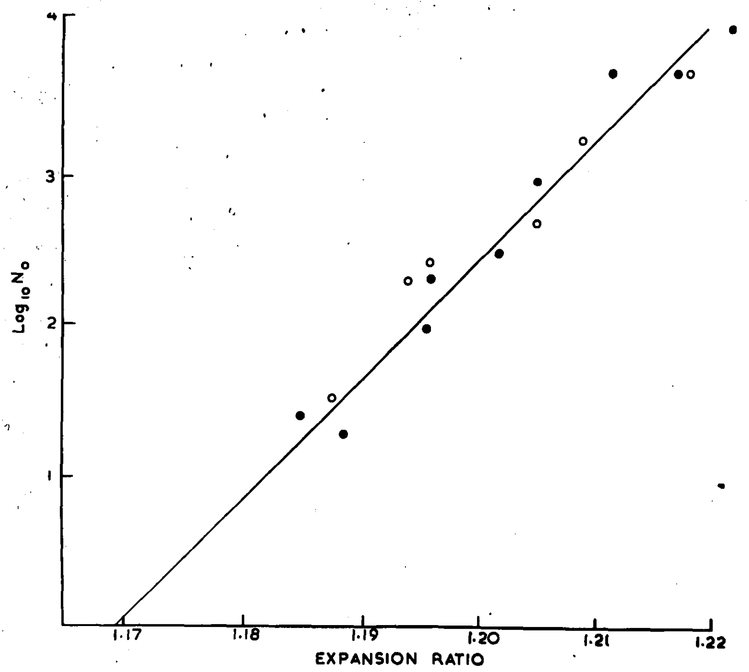


Figure 7. Variation of drop density with expansion ratio, observed with ethyl alcohol and air in the small chamber. Open circles, with ultra-violet light; full circles, with no radiation.

Table 7. Number of Nuclei with Mixtures of Water and Ethyl Alcohol

Percentage Water (by vol.)	Number of Nuclei per cm^3
100	5000
30	3000
10	1000

It will be seen that the number of nuclei increases with the concentration of water in the mixture. As the estimate of drop density was only approximate, it was not possible to determine whether the number of nuclei was proportional to the partial vapour pressure of the water. The above experiments do indicate, however, that the nuclei present in the small chamber arise in some way from the water. The nature of these nuclei will be examined later.

Since the small chamber with alcohol as condensant contained no appreciable contamination, it proved to be very useful for studying the nature of the nuclei produced in the rubber-diaphragm chamber. The experiments done with the small chamber to investigate the source of these nuclei, will now be described.

Nuclei Arising from Large Expansion Chamber

It was firstly verified that the substance produced in the large expansion chamber would also cause condensation in the small chamber on radiation. For this purpose the large chamber was filled with air (the velvet being wet with absolute alcohol) and allowed to stand for several days. It was checked that the small chamber containing absolute alcohol and room air did not show any increased condensation on exposure to ultra-violet light. The small cloud chamber and the manometer reservoir were then filled with the contaminated air from the large expansion chamber. After clearing the chamber from dust particles, it was exposed to ultra-violet light for 30 seconds, and expanded. With an expansion ratio of 1.21 a dense cloud was produced, containing more than 10^4drops/cm^3. In the absence of any radiation, this expansion ratio resulted in a faint cloud, containing less than 10^3 drops/cm^3.

With further irradiations and expansions, the density of the ultra-violet cloud decreased rapidly, indicating that the contaminating substance was being removed. This removal process was demonstrated by filling the chamber with contaminated air and irradiating for 15 minutes. After this time, no increased condensation could be observed on exposure to ultra-violet light. If the chamber was not exposed to ultra-violet light after filling it with contaminated air, then the contamination would persist for an appreciably longer period.

The experiments were repeated using water as condensant in the small cloud chamber. A very dense cloud was obtained after exposing the contaminated gas to ultra-violet light. This cloud contained more than 10^4 drops/cm^3, and was much denser than obtained with room air and water under similar conditions. It was also checked that air which had only been in the large chamber for a few minutes, produced too few nuclei to be detected in the small chamber.

These experiments showed clearly that the condensation nuclei were due to some contamination arising from within the large expansion chamber. The question then arose as to which of the materials present in the chamber was responsible for the production of the contamination. An investigation was therefore made into the conditions under which the contamination was formed. For this purpose, the procedure was to confine some fresh air in a volume containing different materials for periods of at least 24 hours. To detect whether the contamination was then present, this air was then drawn into the small chamber containing absolute alcohol as condensant. The chamber was then exposed to ultra-violet light and expanded, using a ratio which would produce a background drop density of a few hundred per cm^3.

In the first experiment some dry air was put into the large expansion chamber which had been dried carefully. After a few days the contamination was found to be present. This experiment showed that it was not produced by a reaction between the liquid and the materials inside the chamber. Next, the velvet was removed from the chamber, which was then filled with fresh air and sealed off. After a few days it was found that the contamination was present, showing that the velvet could not have been the primary source of the contamination. This left the rubber diaphragm as the most likely source. To check this suggestion, a confined space was constructed in which only rubber and glass came into contact with the air. This was done by clamping down the glass cylinder, sealed off above by the top glass plate, on to a sheet of rubber of the same material as the diaphragm. It was found that the contamination was produced in air which had been confined in this volume for a few days.

These experiments thus showed that the rubber diaphragm is the probable source of the contamination. Further evidence for this conclusion will be presented later.

Further Experiments with Water

The nuclei observed with water and air in the small chamber was shown to arise in some way from the water itself. The above results suggested that these nuclei might be due, however, to some contamination in the water, and not as a result of light absorption by the water vapour. A further series of experiments was therefore made to investigate this question.

If the nuclei were due to light absorption by the water vapour, then it could be expected that the number of nuclei formed would vary with the vapour pressure of the water. The chamber was therefore surrounded by a glass cylinder through which water at a convenient temperature could be passed. The cylinder had a quartz window for admitting the ultra-violet light into the chamber. It was found that the water surrounding the chamber transmitted sufficient light to produce a marked increase in the condensation. When the temperature of the chamber was 8.5°C, the number of nuclei was estimated to be of the order of $2000/cm^3$. At 40°C no definite increase in the number of nuclei could be noticed. The vapour pressure increased by a factor of 7, however, so that if the number of nuclei increased in proportion, they would have produced a definite dense cloud. It therefore seemed unlikely that the nuclei were formed as the result of absorption of light by the vapour.

The same conclusion was also reached from a study of the effect of introducing filters of various liquids into the beam. The absorbing liquids, in layers of 1 cm thickness, were contained in a quartz cell. The equilibrium numbers of nuclei for different filters are shown in Table 8. The approximate wavelength limits of transmission were taken from Brode (1926).

Table 8. Number of Nuclei with Various Absorbers in the Beam

Absorber	Approx. Lower Transmission Limit (A.U.)	Number of Nuclei/cm^3
No		10000
Absolute Alcohol	2200	5000
Carbon Tetrachloride	2600	1000
Benzene	2750	500
Acetone	3250	-

As the number of nuclei decreased gradually with the limiting wavelength transmitted, it was not possible to determine a critical wavelength just sufficient for the production of nuclei. With acetone too few drops were formed to give condensation which could be noticed above the background. A relatively large number of nuclei was produced, however, when the wavelength of the light limited to above 2200 A.U. It thus seemed most unlikely that the effect could be due to light absorption by the water. Water only begins to absorb at wavelengths below 2000 A.U. (Rollefson & Burton, 1939). It was also noted that the the variation in the condensation produced by light of different wavelengths, was very similar to that observed in the large chamber. This suggested that the nuclei in the small chamber might be due to a contaminating substance of the same nature as that in the large chamber.

Nature of Contamination

To verify the conclusion that the nuclei were due to some contamination, various cleaning procedures were tried to see if the impurity could perhaps be eliminated from the chamber.

With some freshly boiled distilled water as condensant, no marked decrease in the number of nuclei was observed. It was noticed, however, that after this water had been left in the chamber for a few days, the number of nuclei increased by a factor of 3, approximately. This suggested that at least some of the nuclei arose from a substance produced inside the chamber. By repeatedly washing the chamber with tap water, a stage was reached where the ultra-violet light produced less than 500 nuclei/cm^3. It was checked that this reduction (by approximately a factor of 10) was not the result of a decrease in the light intensity. This was done by admitting some contaminated air into the chamber. On irradiation, this air again produced a dense cloud at an expansion ratio corresponding to a relatively small background.

The most likely source of the contamination seemed to be the rubber stopper at the bottom of the chamber. An experiment was made to see if an increase in the number of nuclei would be produced by leaving water in contact with rubber. Some tap water, which with the clean chamber would have given rise to very few nuclei, was put into a closed flask containing a sheet of rubber, and left for a few days. On putting this water into the chamber it was found that after irradiation and expansion, a dense cloud was produced, corresponding to the presence of more than 10^4 nuclei/cm^3.

It was therefore concluded that most of the nuclei (if not all) formed in the small chamber also arose from a contamination. Even if pure water was used as condensant, some impurity would still be introduced by the rubber stopper in contact with the liquid.

Experiments with Other Liquids

McHenry & Twomey (1952) have suggested that the nuclei formed in air may be due to the presence of ammonia as an impurity. This suggestion was investigated by operating the chamber with a dilute aqueous solution of ammonia. On irradiation and expansion, a very dense cloud was observed in the chamber. It was noticed, however, that with ammonia the ultra-violet light produced nuclei which formed drops on slow expansions. The effective supersaturation reached during such a slow expansion was rather small, so that the 'nuclei' were quite large. These large nuclei might be of the same nature as observed by Wilson (1899) in his investigation using intense radiation. The production of the large nuclei was stopped when a filter of benzene was introduced into the beam.

Although the ammonia produced a marked increase in the condensation, it does not yet follow that the effect in air is due to ammonia contamination. To investigate this point, the chamber was operated with a dilute solution of hydrochloric acid as condensant. It was found in this case that the ultra-violet light produced approximately the same number of nuclei as with pure water. This experiment showed that the contamination responsible for the nuclei in air and water was not ammonia.

The chamber was also operated with lime water as condensant. In this case the number of nuclei produced by the ultra-violet light again did not differ significantly from that with pure water. Thus the contamination was apparently not affected by the acids or alkalis.

DISCUSSION

In the careful investigation undertaken above, many properties of the nuclei formed by the action of ultra-violet light, have been discovered. It was found, for instance, that the nuclei are produced by some contamination introduced by the rubber necessarily present in cloud chambers. The actual compound responsible for the effect has not yet been identified. Since it is probably evolved from the rubber in minute quantities, the analysis is difficult, but it should be possible to isolate the compound eventually. Once the compound has been identified, there arises the possibility that the effect could be used to detect minute quantities of it.

It has also been discovered that the drops condense on single nuclei, so that at high supersaturations the stage could be reached when all the nuclei caused condensation. In this respect, the nuclei are very similar to ions, but it is known that they are not charged. It can be expected that the nuclei consist of some molecules or free radicals surrounded by an aggregate of vapour molecules. This aggregate will therefore promote condensation at sufficiently high supersaturations. At this stage, it is not possible to give a more complete picture of the structure of the nuclei.

PART IV

A STUDY OF THE OPERATION OF DIFFUSION CLOUD CHAMBERS

INTRODUCTION

Expansion cloud chambers have always suffered from the disadvantage that they can be made sensitive to ion tracks for only a small fraction of the operating time. After the adiabatic expansion, the supersaturation becomes too small for condensation on ion tracks in a time which is of the order of 0.05 sec for a typical cloud chamber. It is then usually required to make a series of slow expansions in order to clear the chamber from all the small drops arising from the fast expansion. Thus the cycling time of a chamber operating at atmospheric pressure, for instance, is of the order of a few minutes.

The efficiency of expansion chambers may be improved by techniques which either decrease the cycling time or prolong the sensitive time. For the study of rare events, however, the idea of continuously maintaining a supersaturation high enough for condensation on ion tracks has always been attractive. Various attempts at constructing continuously sensitive chambers have been made, for instance by Vollrath (1936) who allowed hydrochloric acid and water vapour to diffuse together. No real advance was made, however, until Langsdorf (1939) constructed a continuously sensitive cloud chamber. In the Langsdorf type of chamber, currently referred to as a diffusion chamber, the supersaturation is established in a vapour diffusing from a hot to a cold surface. Under suitable conditions the supersaturation near the cold surface may become high enough for condensation on tracks. Since the vapour is constantly replenished by diffusion, the chamber may become continuous in its operation.

The Langsdorf chamber was of a rather complicated design, and the track quality compared poorly with that obtained in expansion chambers. Recently the interest in diffusion chambers has been revived, and chambers of simpler design which gave better results have been described by Cowan (1950), Miller, Fowler & Shutt (1951) and Needels & Nielsen (1950). Prior to these publications, verbal reports of the success obtained suggested an investigation of the diffusion chamber technique. A short account of the early experience with a diffusion chamber has been published (Barnard & Atkinson). Since then reports of the operation of diffusion chambers have also been given by Choyke & Nielsen (1952), Crewe & Evans (1952), Harteck & Hertz (1952), Munyon & Kurbatov (1952), Nielsen, Needels & Weddle (1951), Shutt et al (1951), Snowden & Bevan (1953) and Succi & Tagliaferri (1952), and a review article has recently been written by Snowden (1953).

In the next section the principles of operation of diffusion chambers will be discussed. With the aid of these and the experimental observations, it is then possible to establish the optimum conditions for condensation on tracks. A description is then given of the cloud chambers designed for operation near atmospheric pressure. In the final section the relative merit of the diffusion chamber technique is discussed.

OPERATION PRINCIPLES

The operation principles of diffusion chambers will now be discussed, with particular reference to chambers in which the hot vapour supply is at the top, so that the vapour is diffusing downwards. Most of the chambers constructed so far have been of this type, and they seem to be in general more satisfactory than the upward diffusion chambers. The operation of diffusion chambers will be considered in a later section.

Simple Theory

The basic design of a diffusion chamber is illustrated in Figure 1. The heated chamber top has a convenient vapour source, such as a trough containing liquid or a wet pad. The chamber is illuminated through the side walls which are sealed to the top and base. Vapour diffusing from the top condenses on the cooled bottom plate.

The basic principle of operation of a diffusion cloud chamber may be understood by considering a chamber for which the following simplifying conditions

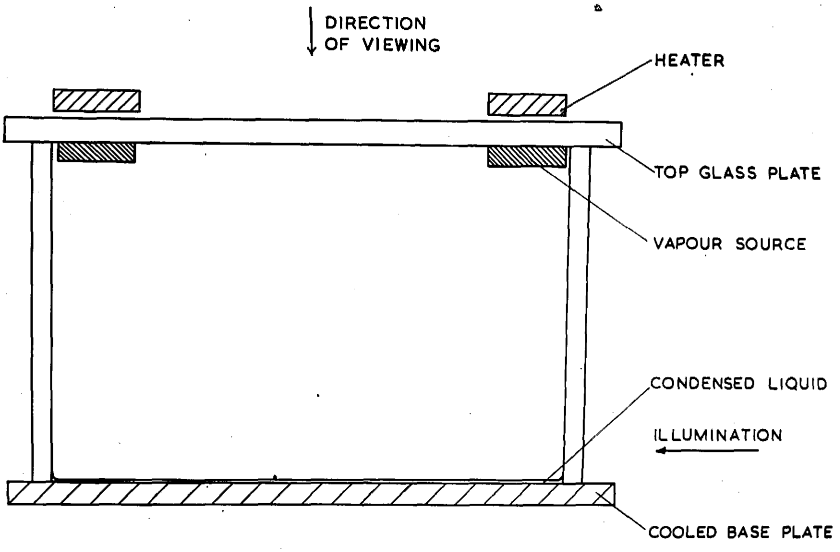


Figure 1. Basic design of a diffusion chamber.

hold. The chamber is supposed to be large enough so that the effect of the side walls can be neglected. It is further assumed that the formation of drops does not disturb the vapour pressure and temperature conditions in the chamber. Finally, the coefficients of heat conductivity and diffusion are considered to be constant over the chamber, and the heat transport due to the vapour flux neglected.

Under these conditions, bothe the temperature and the actual vapour pressure in the chamber will simply be linear functions of the height above the bottom. The boundary condition satisfied by the vapour pressure is that the vapour must be saturated at the top and the bottom of the chamber. The supersaturation can thus easily be determined from the curve showing the variation of the saturated vapour pressure with temperature, as shown in Figure 2. The actual vapour pressure is simply given by the straigth line joining the points corresponding to the top and bottom temperatures. The supersaturation at each point in the chamber is then given by the ratio of the ordinates of the two curves.

The supersaturation calculated in this way

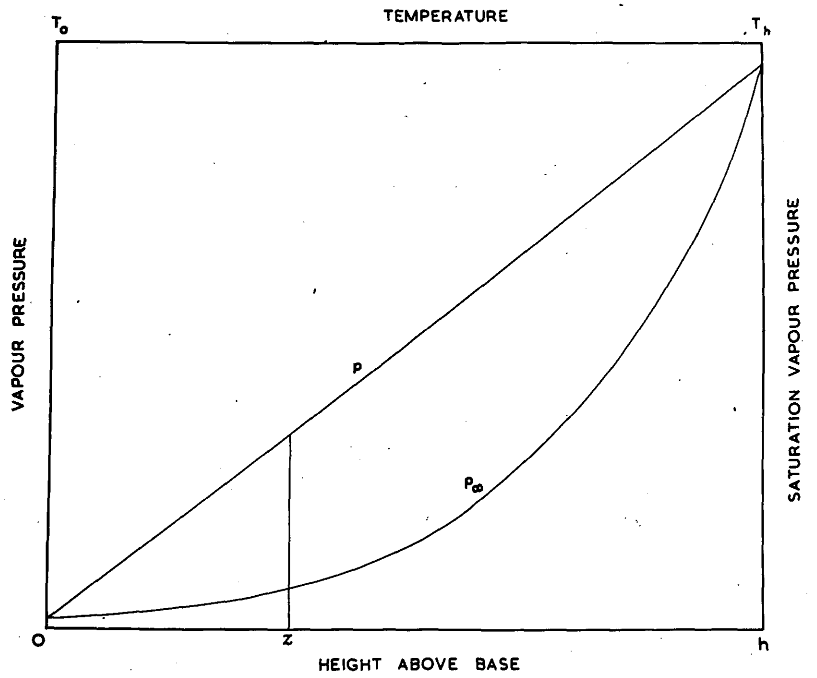


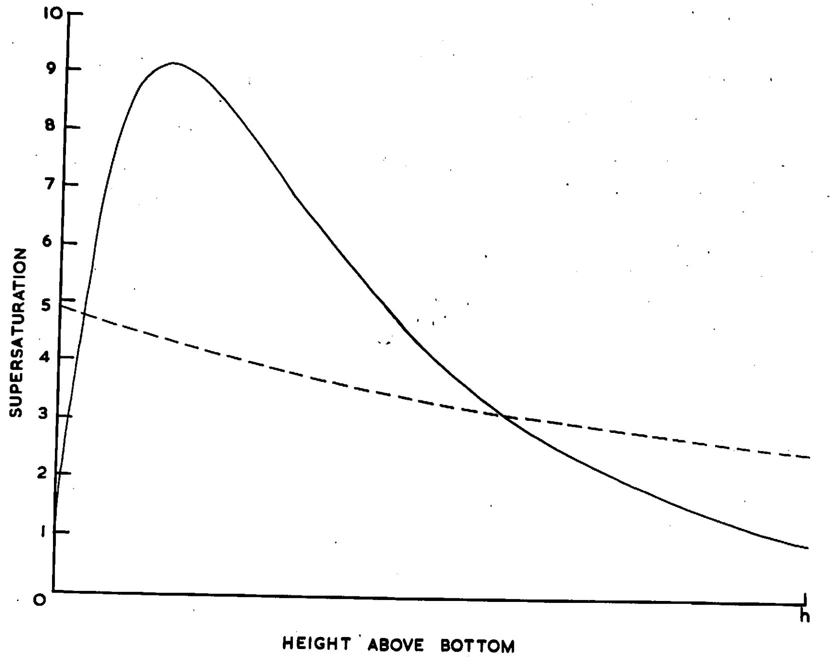
Figure 2. Illustrating the calculation of supersaturation in the chamber from vapour pressure curves.

gives a curve with a maximum near the bottom of the chamber, as shown by the full line in Figure 3. The dotted curve in the figure represents the approximate supersaturation S_c required for condensation on tracks, as calculated from Equation (48) in Part I,

$$\ln S_c = \frac{2M\sigma}{RTd}\left(\frac{4\pi\sigma}{e^2}\right)^{1/3} . \qquad (1)$$

In this equation M is the molecular weight, σ the surface tension and d the density of the liquid, T the absolute temperature, R the gas constant and e the electronic charge. It follows that in the region between the two points of intersection of the curves, the chamber will be sensitive to tracks.

Under the conditions used in operating diffusion cloud chambers, the simplifying assumptions made above are not really justified. Thus for example the variation of the coefficients of heat conduction and diffusion over the temperature range used, must be taken into account. Furthermore the quantities of heat transported by the vapour and liberated by the condensation, are not negligible. The vapour pressure will also be decreased by condensation of the drops and diffusion to the walls. Therefore the vapour



<u>Figure 3.</u> Expected supersaturation distribution (full line) and supersaturation required for ion condensation (dotted line).

pressure and the temperature will deviate considerably from a linear relation with heigth, so that the above method can only be used to give an indication of the conditions that prevail inside a diffusion chamber. The method is quite useful, however, for comparing the supersaturations that can be expected under different conditions.

More Detailed Theory

Langsdorf (1939) has given a more detailed theory of the supersaturation and temperature inside a diffusion cloud chamber, taking into account the variation of the diffusion and heat conduction coefficients with temperature. He still finds it necessary to neglect the effect of the side walls, and uses the one-dimensional equations of diffusion and heat conduction. In his treatment the effect of condensation on the supersaturation is also neglected. A critical review of the Langsdorf theory will now be given, insofar as it is required for the understanding of the operation of diffusion chambers under different conditions. A few errors appearing in his treatment will be corrected.

Langsdorf considers the chamber to be in the steady state, so that there is a constant mass flux of vapour of c gm/cm^2sec, and a constant energy flux of H cal/cm^2sec. Then

$$H = cCt_z - K\frac{dt_z}{dz}$$

$$= cCt_z - K_o(1 + bt_z)\frac{dt_z}{dz} \quad , \qquad (2)$$

where C is the specific heat of the vapour at constant pressure, $t_z = T_z - T_o$, T_z being the temperature at a height z from the floor and T_o the floor temperature, and $K = K_o(1 + bt_z)$ the heat conductivity of the gas mixture, assumed to increase linearly with temperature.

By integration of (2), the temperature distribution with height is found to be given by

$$\frac{z}{h} = \frac{bt_z + (1 + fbt_h)\ln(1 - t_z/ft_h)}{bt_h + (1 + fbt_h)\ln(1 - 1/f)} , \quad (3)$$

where $f = H/cCt_h$, h the total height of the chamber and $t_h = T_h - T_o$, T_h being the top temperature.

To calculate the distribution of vapour in the chamber, Langsdorf assumes that even when the temperature is varying, the isothermal diffusion equations given by Kuusinen (1935) can still be used. Thus, when the steady state is reached,

$$c_1 = (c_1 v_1 + cv)\ _1 - D\, d\rho_1/dz \quad , \qquad (4)$$

where $c_1 = 0$ is the mass flux of the permanent gas, v_1 the partial molar volume of the gas, $v = RT_z/Mp_2$ the partial molar volume of the vapour, R the gas constant, M the molecular weight of the vapour, p_2 the total pressure in the chamber, ρ_1 the density of the gas, and D the coefficient of diffusion of the vapour through the gas. For most vapours the variation of D with temperature can be represented by

$$D = D_o (T_z/T_o)^2 \quad , \qquad (5)$$

where D_o is the diffusion coefficient at T_o and pressure p_2. With this substitution, and changing the independent variable to t_z, using (2), Equation (4) becomes

$$\rho_1 = \frac{MCD_o p_2}{RK_o T_o} \; \frac{ft_h - t_z}{1 + bt_z} \; (1 + t_z/T_o) \; \frac{d\rho_1}{dt_z} \; . \qquad (6)$$

This equation Langsdorf writes in the form

$$p_1 = \frac{MC\ D_o p_2}{RK_o T_o} \ \frac{f t_h - t_z}{1 + b t_h} (1 + t_z/T_o) \ \frac{dp_1}{dt_z} \quad , \tag{6a}$$

by substituting $\rho_1 = M_1 p_1/RT_z$ and $d\rho_1/dt_z = (M_1/RT_z) dp_1/dt_z$, where M_1 is the molecular weight and p_1 the partial pressure of the gas. There is no justification for the last step, however, as the variation in $_1$ due to the temperature variation is not negligible. Now it is not known whether Equation (4) holds for the diffusion at varying temperature, but it seems more logical to retain Equation (6).

Integrating Equation (6) gives

$$\ln \frac{\rho_1(0)}{\rho_1(z)} = \ln \frac{T_z p_1(0)}{T_o p_1(z)}$$

$$= \frac{RT_o K_o}{MCD_o p_2} \left\{ (1 + bft_h) \ln \frac{ft_h}{ft_h - t_z} + (1 - bT_o) \ln \frac{T_z}{T_o} \right\} \tag{7a}$$

The Langsdorf equation gives

$$\ln \frac{p_1(0)}{p_1(z)} = \frac{RT_o K_o}{MCD_o p_2} \left\{ (1 + bft_h) \ln \frac{ft_h}{ft_h - t_z} + (1 - bT_o) \ln \frac{T_z}{T_o} \right\}$$

Langsdorf treats f as a parameter, and proceeds to calculate the supersaturation in the chamber for different values of f. This procedure is meaningless, however, as f is not a variable, but is fixed by the condition that the vapour should be saturated at the top of the chamber. This determines a unique value of f which must be used in (7).

As an example of the numerical results obtained from Equations (7), the supersaturation distribution was calculated for the particular case of methyl alcohol diffusing through air in a chamber with extreme temperatures of -40 and +40°C. The calculated supersaturations are shown in Figure 4, together with that found using the simple method described previously.

It will be seen that there is an appreciable difference in the actual supersaturations, although the shapes of the curves are similar. The maximum supersaturation obtained from the Langsdorf equation (7b) is higher than that given by the simple method, while the more accurate equation (7a) leads to much lower supersaturations.

For methyl alcohol Volmer & Flood estimated that drops will be formed on uncharged molecular aggregates at a rate of about 1 drop per cm^3 per second, at a supersaturation of 3.2 at 270°K. It will be seen that the supersaturations in Figure 4 attain values much

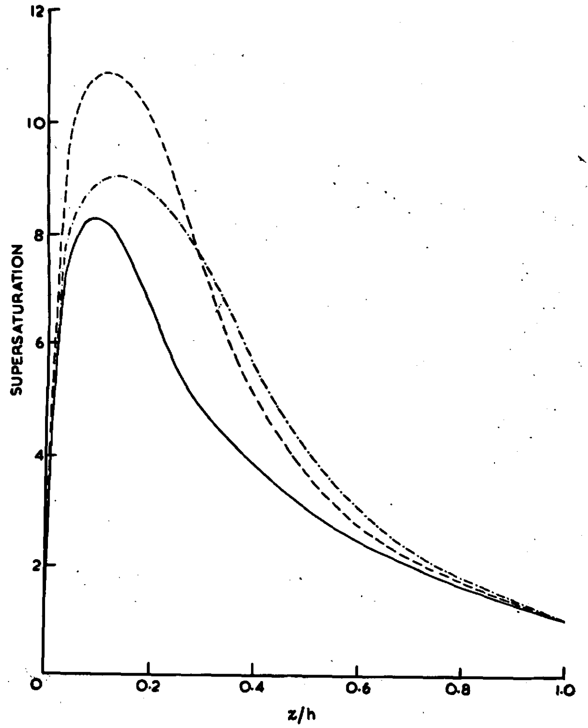


Figure 4. Supersaturation as a function of the fractional height above the floor, calculated from different formulae. Full line, Equation (7a); dashed line, Equation(7b); dot-dashed line, simple method.

in excess of this limit. In a diffusion chamber under the conditions used for the calculation, however, the condensation is observed to take place almost exclusively on stray ions, so that the maximum supersaturation must therfore be less than 3.2. As the actual supersaturation is thus much less than the value predicted by (7a), it is clear that the effects of diffusion of vapour to the walls and of condensation are not negligible. Condensation at the walls will keep the vapour just saturated there, so that there will be a continuous flow of vapour outwards. Of probably more importance is the effect of the drops formed on stray ions. As these drops grow, they remove vapour from the chamber, and also liberate heat, both effects resulting in a decrease in the supersaturation. An accurate estimate of the supersaturation in the chamber can only be made by taking into account these effects. Equation (7a) is, however, very useful in comparing the supersaturations that may be expected from different conditions in the chamber.

Effect of Condensation

Succi & Tagliaferri (1952) have attempted to extend the theory of Langsdorf to take into account the effect of condensation. They estimate the vapour removed and the heat liberated and give modified curves for the supersaturation. In their calculation it is assumed that the supersaturation depends simply on the temperature and the vapour flux, so that the supersaturation with condensation is assumed to be equal to the supersaturation in the absence of condensation corresponding to the reduced flux. As there is no simple relation between the vapour pressure and the flux, this procedure is not valid. Moreover, as pointed out above, even in the absence of condensation, the values predicted by Langsdorf are probably too high. Thus the supersaturation may differ substantially from that obtained by the method of Succi & Tagliaferri.

A more detailed theory of diffusion chambers has been given by Shutt (1951) who considers the effect of condensation, but still neglects the diffusion to the walls. Using the one-dimensional equations of diffusion and heat conduction as modified by condensation, he calculates the temperature distribution required to get a given sensitive depth in the chamber. The temperature distribution is obtained as the solution of an integral equation which is solved numerically for the case of methyl alcohol under different conditions. To maintain the required temperature distribution, a certain amount of heat has to be supplied or removed at each level in the chamber. Shutt suggests that this may be done by a process of slow convection of the gas, continuously exchanging heat at the walls. The temperature of the walls may differ from that in the centre by a considerable amount, depending on the size of the chamber. As Shutt does not estimate the temperature distribution of the walls, his results are not in a useful form for the practical operation of diffusion chambers. The estimate of the wall temperature requires, however, solutions of the three-dimensional diffusion and heat conduction equations. It may be remarked that Shutt uses Equation (1) for the critical supersaturation required for ion tracks. Now it has been pointed out in Part I that for methyl alcohol, even the 'critical supersaturation' for condensation on ions to become noticeable, is much in excess of the value predicted by Equation (1). Thus Scharrer (1939) observed a critical supersaturation of 2.95, as compared with the theoretical value of 2.07. The supersaturation required for the formation of sharp tracks will be even higher than the critical value. Hence the temperature estimate of Shutt must be regarded as only approximate.

Conclusion

There is thus no accurate theory which gives the supersaturation and temperature distributions in diffusion chambers under different conditions. An accurate estimate of the conditions in the chamber is, however, very complicated, and its usefulness may be questioned. From a practical point of view, all that is required is to be able to determine the optimum conditions for operation. Fortunately, this may be done from simple considerations .

OPTIMUM CONDITIONS FOR OPERATION

In this section the optimum conditions for the operation of diffusion chambers will be examined, firstly with reference only to the downward diffusion type. The modifications in the operation principles of upward diffusion chambers are considered later. The discussion is made on the basis of the simple theory given above and the experience gained in operating diffusion chambers. Although the discussion is thus necessarily only qualitative, it is useful to have some guide for the operation of diffusion chambers.

To obtain the best performance of the chamber, the conditions that may be varied include the height ofthe chamber, the vapour used, the gas and total pressure in the chamber, the temperature distribution and the electric field conditions. The effect of these factors on the supersaturation will be considered in turn.

For the succesful operation of a diffusion chamber, it is important that the gas should not show large convective motion, otherwise the tracks will become distorted. The total gas density must therefore increase downward if the gas in the chamber is to be stable.

Height of the Chamber

As long as the effects of drop-wise condensation and vapour diffusion to the walls can be neglected, the supersaturation and temperature will depend only on z/h, the fractional height above the floor. It thus seems as if the depth of the region which is sensitive to tracks will simply be proportional to the height of the chamber, other things being equal. It was observed, however, that when the height of the chamber was increased, the sensitive volume did not increase in proportion, while the track quality became poorer.

The explanation of this effect is that both the vapour removed and the heat liberated by the growing drops falling through the sensitive region will increase with drop size. If the sensitive height is increased, the larger drops falling through the lower part of it, may have a great disturbing effect on the supersaturation. Thus it is a general rule that increasing the sensitive depth will impair the track quality. In practice a compromise must be made between the height of the sensitive volume and the track quality. A sensitive depth of about two inches was found to be convenient, as this depth could be illuminated adequately.

It is best to use a chamber with the minimum height for which the required sensitive depth can be attained, for the following reason. The ions formed in the insensitive region at the top of the chamber stray into the sensitive volume, where they form an undesirable background and impair the track quality. The number of these background drops will be reduced to a minimum when a shallow chamber is used. Using methyl alcohol diffusing through air at atmospheric pressure, a sensitive depth of two inches could easily be obtained with a chamber of total height of 4 inches.

Choice of Vapour

Most of the diffusion chambers constructed so far operated very satisfactorily with methyl alcohol vapour. It was decided, however, to investigate carefully whether other liquids might not even give better results.

A liquid can only be used in a diffusion chamber if it has a suitable vapour pressure curve so that on the application of a convenient temperature gradient, it will give a supersaturation which is large compared with the value required for condensation on ions. Bearing this consideration in mind, the properties of a number of liquids were examined.

The critical supersaturations for condensation on ions for a variety of liquids as measured by Scharrer (1939), are quoted in Table 2, Part I. It will be seen that the liquids with the lowest critical supersaturations are ethyl alcohol (1.94) and methyl alcohol (2.95). Figure 5 compares the supersaturations calculated from Equation (7a) for ethyl and methyl alcohol respectively, diffusing through air at atmospheric pressure, between temperature limits +40 and -40°C. The supersaturations expected for ethyl alcohol compares favourably with that for methyl alcohol, when the lower critical supersaturation of the former is taken into account.

The operation of a diffusion chamber with ethyl

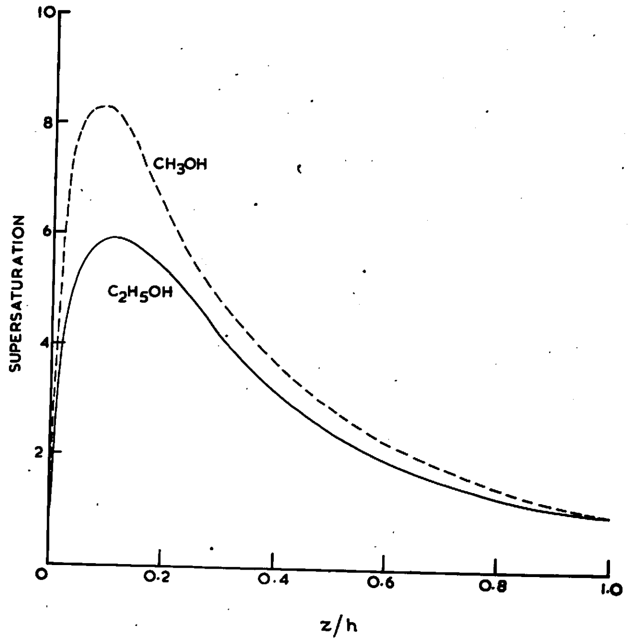


Figure 5. Supersaturation as a function of height in the chamber, for methyl and ethyl alcohol. Air at atmosperic pressure, temperature limits -40 and + 40°C.

alcohol was therefore investigated experimentally. It was found that with a chamber filled with air at atmospheric pressure, top temperature 40°C, bottom temperature -50°C, a sensitive depth of about one inch was obtained. With methyl alcohol in the chamber under approximately the same conditions, the sensitive region was just over two inches. The use of methyl alcohol was therefore preferrred, though with an increased top temperature a comparable sensitive depth could probably be obtained with ethyl alcohol.

The possibility of using the other liquids mentioned in Table 2, Part I, was also considered. From their vapour pressure curves rough estimates were made of the maximum supersaturation that could be expected over a usable temperature range. It was found that for none of these liquids the maximum supersaturation was big enough compared with the critical supersaturations to promise satisfactory operation of a diffusion chamber.

For more complex organic liquids, Equation (1) may be used to give an indication of the supersaturation required for track formation. Since the density and the surface tensions of these liquids do not differ appreciably from that of the alcohols, while their molecular weights are significantly higher, they can be expected to have correspondingly higher critical supersaturations. The usual shapes of the saturation vapour pressure curves of these liquids do not indicate that a sufficiently high supersaturation could be reached. Another consideration is that for most liquids (including water) the bottom temperature required is below the freezing point of the liquid, with the result that the bottom of the chamber will become covered in a layer of ice, making photography difficult. It is thus unlikely that a pure liquid will be found which will give better operation than the alcohols.

A possibility which has not yet been fully investigated is the use of mixtures, and in particular mixtures of the alcohols with water. It is well known that the critical supersaturation required for mixtures are less than for the pure liquids. The properties of mixtures are not well enough known to decide whether using a suitable mixture will improve the operation of a diffusion chamber. The experimental evidence is inadequate, but it seems as if the possible improvement in operation does not justify the added difficulty. Thus Cowan (1950) found the greatest sensitive depth with mixtures of ethyl alcohol, methyl alcohol and water. The composition of the mixture was changed by evaporation, however, so Cowan preferred to use methyl alcohol.

Temperature Distribution

From the shape of the vapour pressure curves it can be expected that the supersaturation in the chamber can be increased by lowering the bottom temperature. This result is verified by the more detailed theory. Thus Figure 6 shows the supersaturations calculated from Equation (7a) for methyl alcohol diffusing through air at atmospheric pressure, for the temperature ranges -40 to +40°C and -50 to +30°C. It will be seen that the operation of the chamber is very sensitive to changes in the bottom temperature. The most convenient way of cooling the bottom is to use solid carbon dioxide. There must therefore be an efficient cooling system to ensure the lowest possible bottom temperature. A bottom temperature of

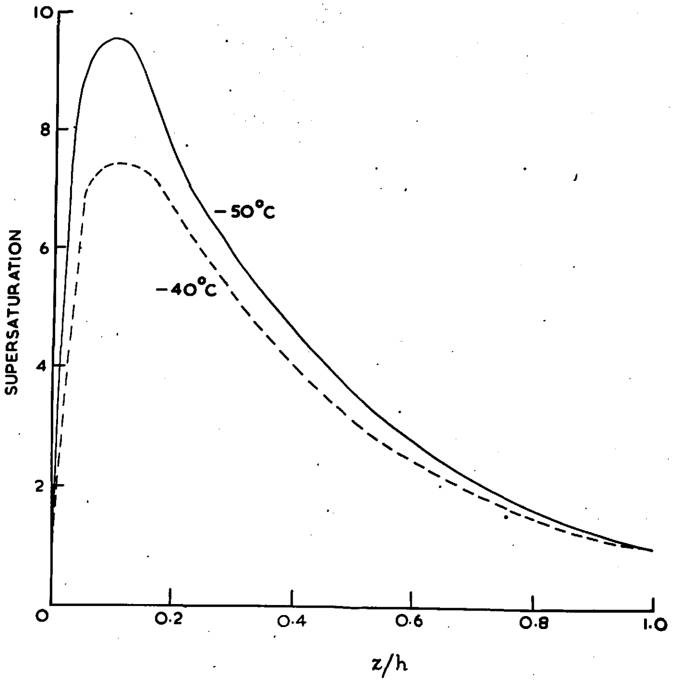


Figure 6. Supersaturation as a function of height, for methyl alcohol and air at atmospheric pressure, temperature ranges -50 to +30°C, and -40 to +40°C.

at least -50°C was found to be advisable for good track quality.

The supersaturation can also be increased by increasing the top temperature, but the operation is not so sensitive to changes in top temperature. The top temperature cannot be increased indefinitely, however, for the following reasons. If the vapour is denser than the permanent gas, then the top temperature will be limited by the stability condition which is only possible to satisfy if the vapour pressure is sufficiently small at the top. Even if the vapour is lighter than the gas, it is nevertheless advisable to keep the top temperature well below the boiling point of the liquid. Thus Langsdorf (1939) observed a rain of large drops formed at the top of the chamber, where they could upset the conditions sufficiently to stop the chamber from operating. It is not clear how these small drops arose, but they might just have been due to a spray of small drops produced by the boiling.

In the absence of leaks no such general rain as described by Langsdorf was observed here, presumably because the top temperatures used were not high enough.

In the chambers operated here with methyl alcohol in air at atmospheric pressure, the top temperature was limited by the consideration that if the sensitive depth was increased, the track quality would deteriorate. It was thus found best to adjust the top temperature to give a sensitive depth of only about two inches. With a bottom temperature of about $-50^{\circ}C$, the corresponding top temperature was about $40^{\circ}C$.

The operation of a chamber may perhaps be improved by the application of a suitable temperature gradient to the walls. The effect of a controlled wall temperature is, however, very difficult to estimate theoretically. It was found experimentally that when the wall temperature was increased in the upper half, the performance of the chamber seemed to improve slightly, though it was difficult to ensure that the other conditions were kept unaltered. In any case, the wall temperature has only a small effect in the shallow chamber, presumably because the temperature in the middle of the chamber is mainly determined by the top and bottom temperatures. It was therefore not considered worthwhile with this chamber to have the added difficulty of controlling the wall temperature.

Choice of Gas and Pressure

According to the simple theory, the operation of the chamber should be independent of the permanent gas used. Even in the absence of condensation, the more detailed treatment shows that the supersaturation will depend to some extent on the permanent gas, due to the different values of the coefficients of diffusion and heat conduction. For most experiments in nuclear physics, however, the choice of the gas is prescribed by the experiment, and therefore only the pressure can be varied for the best operation of the chamber.

Even neglecting condensation, the supersaturation in the chamber will depend on the gas pressure. This is illustrated in Figure 7, which shows the supersaturations calculated from Equation (7a) for methyl alcohol and air at different pressures. It will be seen that at higher pressures the curve tends to flatten out, leading to lower maximum supersaturations and consequently to inferior tracks.

At higher pressures there is also another effect which will limit the operation of the chamber, as noted by Shutt (1951). Shutt points out that the

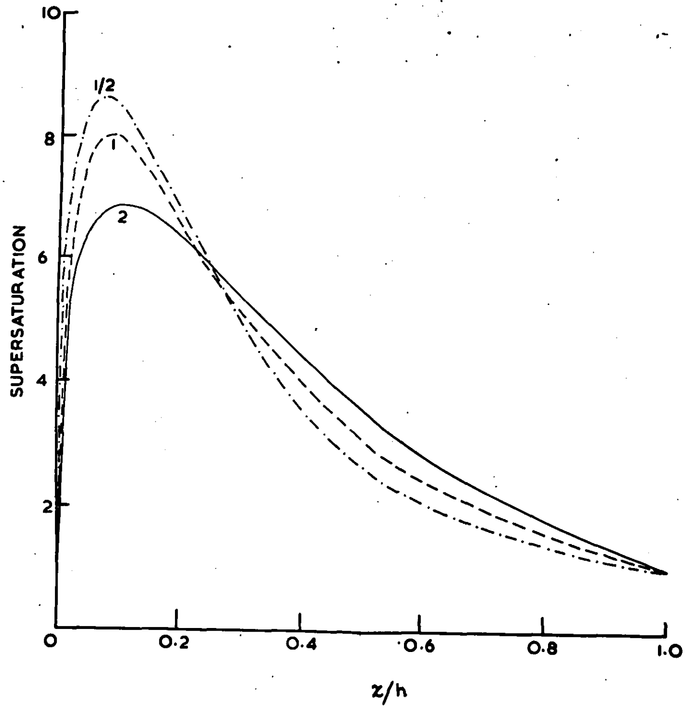


Figure 7. Supersaturation as a function of height, for methyl alcohol, temperature limits -40 and +40°C, air at pressures of ½, 1 and 2 atmospheres.

ionic background will be increased at higher pressures, with a subsequent deterioration of the conditions inside the chamber. In fact, Shutt has estimated that for air and methyl alcohol the chamber will stop operating with the normal cosmic ray background at pressures of 3 to 4 atmospheres.

The condition of stability determines a lower limit to the gas pressure that can be used, for a particular combination of vapour and gas, and for a given temperature distribution. Therefore the chamber will only operate satisfactorily over a limited pressure range for each gas.

Electric Field Conditons

The operation of diffusion chambers has so far been considered in the absence of an electric clearing field. It was realised, however, that the performance of the chamber could be improved considerably by the proper use of a clearing field. The effect which an electric field has on the operation of the chamber will now be described.

Due to cosmic rays and radio-active contamination, ions will be formed continuously in the insensitive part of the chamber. In the absence of an electric field, the number of these ions gradually build up to the equilibrium value, which is reached when the number of ions removed by diffusion and recombination is equal to the number produced. Consider now the action of a vertical clearing field applied between the top and bottom of the chamber, the top being positive. When the field is switched on, all the positive ions present in the top part of the chamber is drawn downwards and produce a fairly dense cloud at the top of the sensitive volume. In falling through the bottom half of the chamber, this cloud reduces the supersaturation to below the value necessary for track formation. The chamber is thus made insensitive to tracks, a condition which lasts for a few seconds. This is the time required for the vapour to be replenished by diffusion from the top. When the chamber has recovered, most of the tracks are rather diffuse. The appearance of these tracks is illustrated in Figure 8.

A diffuse track is caused by the passage of an ionizing particle through the top insensitive part of

Figure 8. Appearance of diffuse tracks observed with the field.

the chamber. The vertical field pulls all the positive ions downwards, and where the ion column reaches the top of the sensitive volume a diffuse tracks is produced. The tracks are approximately horizontal, because as soon as the drops form round the ions their mobility is practically reduced to zero. Before condensation sets in, however, the ions do have time to diffuse considerably, and this accounts for the appearance of the track. Tracks formed in the sensitive volume are still relatively sharp, since the drops are formed before the ions have moved considerably. These sharp tracks occur in all directions and tend to be obscured by the more apparent diffuse tracks.

If the field is applied with the top negative, then a marked change in the appearance of the sensitive volume can be noticed. When the field is switched on, the cloud formed on the negative ions, is much fainter than with the positive ions. In fact, this cloud is not dense enough to upset the operation of the chamber appreciably. The tracks drawn into the sensitive volume from above are very diffuse, so that they may be difficult to distinguish. The tracks formed in the sensitive region, however, are again relatively sharp.

The difference in behaviour of the chamber for different field polarities is explained by the fact mentioned in Part I that in methyl alcohol the condensation takes place more readily on the positive than on the negative ions. Under the usual operating conditions the supersaturation in the sensitive volume is just sufficient for condensation to take place on most of the positive ions. At this value of the supersaturation, condensation will take place only on a few negative ions before they are displaced appreciably by the field. A column of negative ions pulled into the sensitive volume will therefore appear very diffuse, as the drops will be formed at different levels.

When the clearing field is removed, some of the ions formed in the insensitive part of the chamber will still reach the sensitive volume by diffusion. The number of ions straying downwards will increase until the equilibrium ion density in the top half has been set up. On reaching the sensitive volume, these ions form undesirable background drops which diminish the supersaturation and thus impair the quality of the tracks.

Bearing in mind the above considerations, the best conditions for sharp tracks may therefore be determined. It must also be remembered that in general the sharpest tracks are always observed in the absence of the field, as the ions are then only moved by diffusion before condensation sets in.

For pulsed operation the best operation of the chamber will be obtained by sweeping out the ions with a clearing field which is switched off a few seconds before the ionizing pulse. This time delay is advisable to allow all the diffuse tracks formed with the field just to fall out. The delay should, however, be kept as short as possible, since the number of background drops increase rapidly when the field is removed.

Condensation on tracks during the ionizing pulse will reduce the vapour density in the chamber, so that the bottom half may become insensitive to tracks immediately afterwards. Hence the clearing field is again applied until the vapour density in the chamber has recovered by diffusion. The recovery time depends on the amount of condensation, but is found to be less than 10 seconds in a chamber with air and methyl alcohol at atmospheric pressure, even for the most intense ionization. When the chamber has recovered the cycle of operations can be repeated. For a chamber at atmospheric pressure, the cycling time can thus be made less than 15 seconds, even for dense ionization.

For pulsed operation the clearing field is merely used to reduce the number of stray ions in the sensitive volume to a minimum, so that the direction of the field is of little importance. A vertical field with the top negative does have the slight advantage that the negative ions drawn into the sensitive volume, are less effective for condensation. The actual magnitude of the clearing field can be varied between wide limits with little change in the operation of the chamber.

The chamber can deal with quite a large pulse of ionizing radiation, but will only operate satisfactorily with a limited amount of continuous radiation. If it is desired to observe a weak radiation continuously, then in the absence of a clearing field the track quality may become rather poor due to the effect of the stray ions from the top half of the chamber. These ions may be prevented from reaching the sensitive volume by applying a field between the top plate and an earthed grid across the top of the sensitive volume. This arrangement has, however, the disadvantage that the grid interferes with the photography and will also upset the supersaturation conditions. For continuous operation it therefore seems best to apply a steady vertical field, the top plate being negative. With this field the diffuse tracks drawn into the sensitive volume are very indistinct, while the tracks formed in the sensitive volume are quite sharp for vertical observation. A horizontal field will prevent stray ions from reaching the sensitive volume, but it has the disadvantage that the tracks will be broadened considerably by the field.

Upwards Diffusion Chambers

Some workers have also obtained satisfactory operation in chambers in which the vapour diffuses from the heated bottom upwards to the cooled top. The properties of these upward diffusion chambers will now be considered briefly, and their performance compared with the more usual downward diffusion type.

In the absence of condensation, the supersaturation expected in these chambers will be identical with that for downward diffusion. In practice, however, the stability requirements presents a difficult problem, as the total gas density must increase downward notwithstanding the increase in the temperature. To achieve this, it is therefore necessary to use a vapour much denser than the gas, so that the increase in vapour density will more than compensate the decrease in gas density with temperature.

For hydrogen or helium near atmospheric pressure it is not difficult to find a suitable vapour. Thus Nielsen, Needels & Weddle (1951) operated a diffusion chamber with propanol vapour diffusing upwards through helium near atmospheric pressure. They remarked that the chamber operated satisfactorily, but that the track quality was inferior to that obtained in downward diffusion chambers. Harteck & Hertz (1952) obtained good tracks with helium and hydrogen near atmospheric pressure in an upward diffusion chamber, using a mixture of 67% ethyl alcohol and 33%

water as vapour source. It thus appears that with the light gases near atmospheric pressure, satisfactory operation can be achieved in upward diffusion chambers.

With oxygen or nitrogen near atmospheric pressure a very heavy vapour is required to give a stable mixture. Thus with nitrogen at 500 mm pressure Harteck & hertz used as vapour source a mixture of 63% ethyl alcohol, 22.5% water and 6.5% pentane, the pentane serving as a stabiliser. It has been pointed out that it is unlikely that the heavy vapours will give better supersaturation conditions than the alcohols. Therefore with nitrogen or heavier gases it is preferable to use a downward diffusion chamber.

DIFFUSION CHAMBER DESIGNS

Various diffusion chambers designed for operation near atmospheric pressure will now be described. These chambers were all of the downward diffusion type, and was normally operated with methyl alcohol and air at atmospheric pressure. A brief description of the experimental chamber has already been published (Barnard & Atkinson, 1952). The operation of this chamber under different conditions has been studied and the principles of diffusion cloud chamber operation understood. It was then possible to improve the design and construct chambers for special applications.

Experimental Chamber

The design of the experimental diffusion chamber is illustrated diagrammatically in Figure 9. Figure 10 shows the actual appearance of the cloud chamber.

The bottom of the chamber consists of a circular brass plate, 12 inches in diameter and 0.3 inches thick. The walls of the chamber are formed by three glass cylinders, each nine inches in diameter and 2 inches high. Six bolts clamp the cylinders between the top and bottom plate. Rubber rings form adequate gaskets between the cylinders and the top and bottom. The top is insulated from the bolts and a reversible field can be applied between the top and bottom. The chamber can be observed through a glass window, 6 inches in diameter, in the top plate.

A ring made up from layers of filter paper covered with velvet and fixed to the underside of the top plate, serves as convenient vapour source.

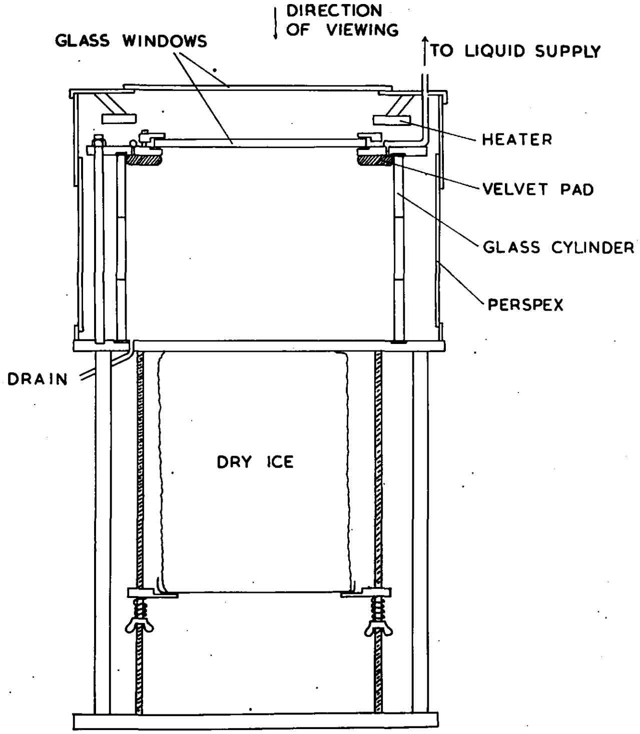


Figure 9. Diagram of experimental diffusion cloud chamber.

Figure 10. Photograph of experimental diffusion cloud chamber.

The liquid in use can be fed to this ring through small holes in an annular brass tube soldered into the top of the chamber. Excess liquid on the bottom of the chamber can be drained off through an outlet at the side of the chamber.

In order to shield the chamber from draugths, it is surrounded by a brass cylinder 12 inches in diameter, with perspex side windows for illumination. A brass cover with large glass window completes the shield. This brass cover also supports the 1000 W heater coil which is suspended 0.5 inches above the top of the chamber. By this arrangement the top brass plate and the glass window is heated uniformly, so that condensation on the top window is prevented.

The chamber is supported on three pillars supported on a brass base. The block of dry ice is pressed firmly against the bottom by a pan supported on three springs. The springs in turn rest on wing nuts, each of which can be screwed up a threaded rod fixed to the base plate. The nuts can thus be continually adjusted to take up the evaporation of the dry ice, so that the tension in the springs can be maintained.

The chamber was usually illuminated by a steady lamp and observed visually. The chamber could also be illuminated with two flash lamps, and photographs taken with a camera supported on the top cover. The chamber bottom is blackened with stove polish. When this surface becomes covered with condensed liquid, it forms an excellent photographic background. Methyl alcohol dissolves the common black paint and lacquers, but has no effect on this surface.

Soon after the dry ice has been put into position and the heater switched on, a dense cloud can be seen in the chamber due to condensation on dust particles. The density of the cloud gradually decreases as the contaminating particles are removed with the drops. After all the dust particles have been cleared out and the supersaturation in the chamber has increased sufficiently, condensation on ions commences in a thin region near the floor. As the bottom of the chamber gets colder, the sensitive region gradually extends further up the chamber. After a period of about half an hour the chamber attains a steady working condition. The top temperature was normally adjusted to give a sensitve volume of about two inches thick, since with higher top temperatures and consequently greater sensitive depth, the track quality was observed to be inferior.

Under these conditions the electron tracks originating from cosmic radiation and radio-active contamination may be seen to form in the sensitive volume. These tracks fall out slowly under the action of gravity. The quality of the tracks may be improved by the periodic application of the clearing field. Immediately after the field has been switched off, the input of stray ions from the insensitive part of the chamber is reduced, so that the tracks in the sensitive volume become sharper. Figure 11 shows a photograph of the appearance of the normal background in the chamber, about 5 seconds after the clearing field has been switched off.

The design of the chamber was quite convenient for the study of the operation under different conditions. The chamber has also been used on numerous occasions as a demonstration apparatus. For the continuous observation, the chamber was usually operated with a steady field, the top plate being negative. Even in the absence of any artificial source, the stray

Figure 11. Random electron tracks observed in diffusion chamber, about 5 secs after the field has been switched off.

electron tracks in the chamber are quite impressive. Occasionally even more striking events can be seen, such as the passage of a stray alpha-particle or the end of an air-shower. The effect of passing a short pulse of X-Rays through the chamber or quickly bringing up a gamma-source to the chamber, are also very instructive.

The chamber in its present form is not, however, well suited for experiments in nuclear physics, as the method of cooling the bottom is rather unsatisfactory. The chamber needs continual attention as the wing nuts have to be adjusted frequently to keep the dry ice pressed firmly against the bottom. Even then, the whole of the chamber bottom can only be cooled adequately if the block of dry ice is fresh. With a block which is a few days old and thus evaporated to a smaller diameter, only part of the chamber can be made sensitive to tracks. It is also clear that the present cooling method cannot be used for bigger chambers.

Refrigerating Unit

A more satisfactory method of cooling the bottom is to keep it in contact with liquid circulating through a refrigerating unit. In the simplest form of refrigerating system the circulating liquid is simply cooled indirectly with dry ice.

Figure 12 illustrates the design adopted for the refrigerating system. The appearance of the unit connected to a diffusion chamber is shown in Figure 13.

Methylated spirits cooled in a large reservoir is circulated round the system with a centrifugal pump. The dry ice cannot be placed directly into this reservoir, since then some of the carbon dioxide evolved will dissolve in the methylated spirits. On reaching the hotter pump, some of the gas escapes thus causing an 'air lock' and stopping the circulation of liquid. Small pieces of dry ice are therefore fed into a slightly smaller container inside the big reservoir. This container has sufficient alcohol in it to ensure good thermal exchange with the circulating liquid.

Since the pump leaked appreciably when it was

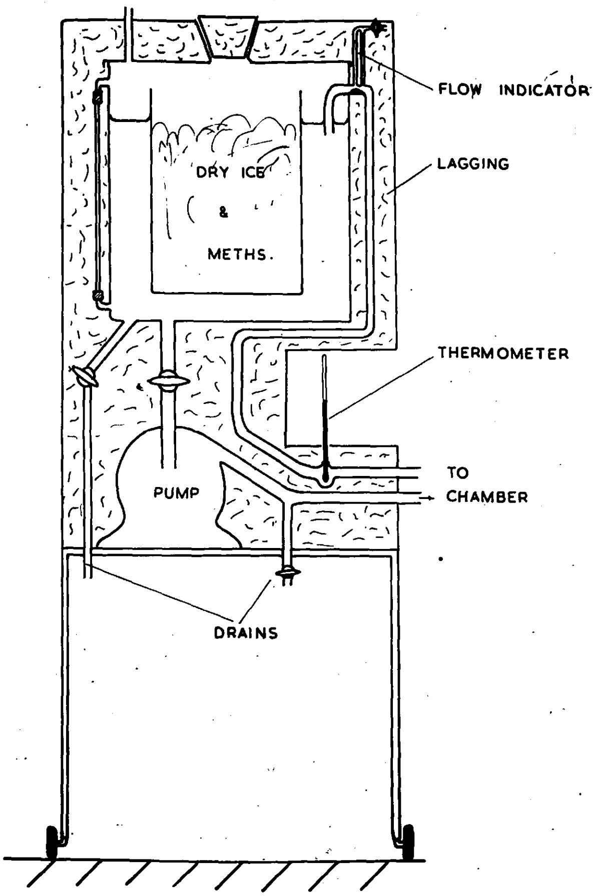


Figure 12. Refrigerating unit.

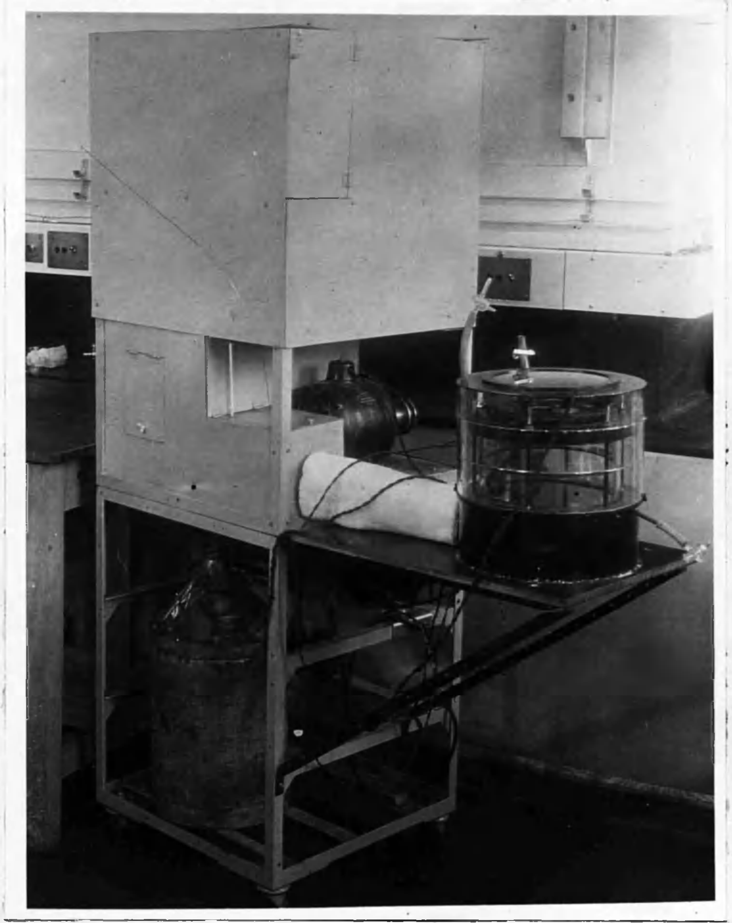


Figure 13. Refrigerating unit connected to the modified cloud chamber.

stationary, a tap is included between it and the large reservoir. The liquid from the system can be drained through two taps at the bottom. Methylated spirits can be replenished at the top, the level of the liquid in the reservoir being shown on a side tube.

An alcohol thermometer indicates the temperature of the liquid returning from the chamber to the reservoir. It is also convenient to have some indication of the rate of flow in the closed system. The flow is estimated by comparing the heights of liquid in two small tubes connected to the inlet pipe, one tube being over a constriction in the pipe.

The whole unit is built on a trolley for easy mobility, and can be connected to different chambers. The reservoir and pipes are well lagged with a layer of cotton wool at least two inches thick. The pump is also completely surrounded by cotton wool, except for the shaft and pulley driven by an electric motor at the side.

The large volume of liquid used for pumping is rather a disadvantage, since the liquid requires about an hour to cool down sufficiently. For this cooling process about 25 pounds of dry ice is required.

Once the liquid has reached the working temperature, however, it needs very little dry ice to compensate the heat losses. For example, if the small container is then filled with dry ice, the system will maintain the temperature for a few hours. A temperature of $-50^{o}C$ could easily be reached with the modified diffusion chamber.

Modified Chamber

Figure 14 shows a diagram of the modified chamber, designed for use in conjunction with the refrigerating unit. A photograph of the chamber connected to the unit is shown in Figure 13.

The cooled liquid is circulated round a tank 1.5 inches deep and 9 inches in diameter, soldered to the bottom of the chamber. The tank has a system of baffle plates which ensures the distribution of the liquid over the whole bottom, which is thus cooled uniformly. The bottom and the tank is adequately lagged with cotton wool.

It has been pointed out that for the same sensitive volume, better operation is obtained with a shallow

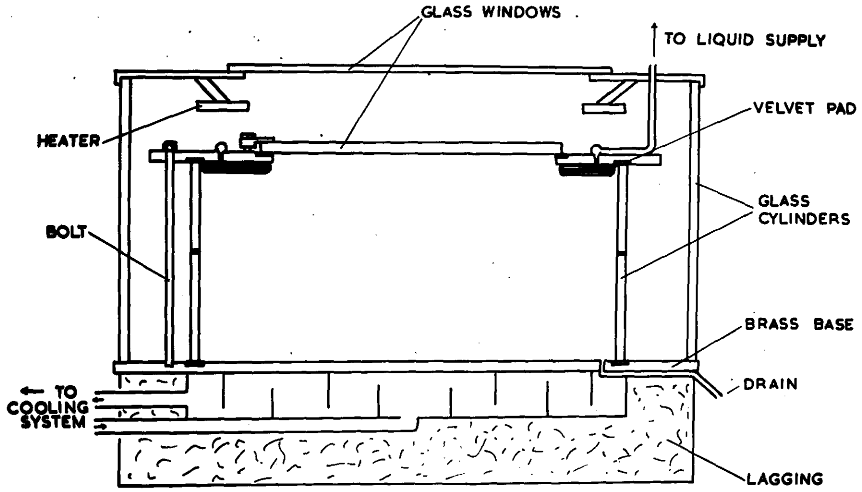


Figure 14. Modified chamber.

chamber, since fewer background ions are formed in it. The height of the chamber was therefore reduced to 4 inches, using only two glass cylinders to form the walls. The outer cover was now built up of three glass cylinders, 12 inches in diameter and 2.3 inches high. The other details of the chamber construction were kept unaltered.

The chamber operates very satisfactorily and good tracks can be observed in it. The sensitive volume extends to about one inch from the walls, showing that the bottom is cooled uniformly. For best track quality, the top temperature was again adjusted to give a sensitive depth of about 2 inches.

Square Chamber

The chambers described above suffer from the disadvantage that a layer of ice soon forms round the bottom cylinder. This ice layer interferes with the illumination, and for photography the effect of light scattered from it may become serious. The area of the sensitive volume is also rather small for track measurements.

For these reasons the design illustrated in Figure 15 was tried. The walls of this chamber are in the form of a rectangular cylinder, with sides 12 inches long and 6 inches high. The cylinder was constructed by Barr & Stroud, from glass plates, $\frac{1}{2}$ inch thick, which were cemented together with 'araldite'. The outer cover, also in the form of a rectangular cylinder, sides 15 inches long and 6 inches high, was constructed in the same way from $\frac{1}{4}$-inch thick glass plates. Both the inner and the outer cylinder are clamped tightly between the top and bottom plates, by eight bolts. Rubber rings, 0.1 inches thick, serve as gaskets between the cylinders and the bottom and top plates. The space between the walls is thus sealed off adequately to prevent the formation of ice on the inside cylinder. The ice that forms on the outside cylinder is not sufficient to interfere with the photography.

The arrangements for heating the top and supplying the vapour are very similar to that used before. The top glass window is a square of sides 9.5 inches, and thus allows most of the sensitive volume to be photographed stereoscopically. The bottom is again cooled

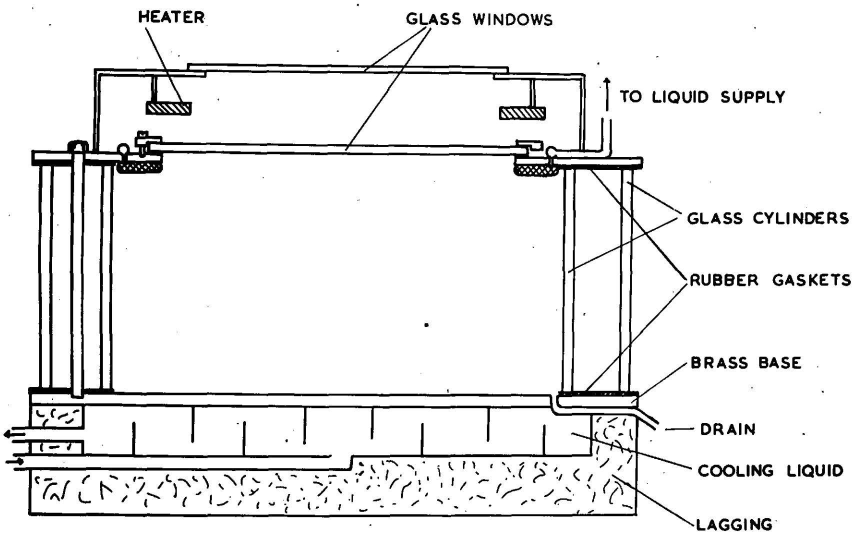


Figure 15. Square Chamber.

by passing methylated spirits from the refrigerating unit through a tank soldered to the bottom.

The chamber operates satisfactorily and sharps tracks can be obtained in it. The design has however the disadvantage that the construction of the chamber walls is quite a difficult problem. The glass plates have to be cemented together very accurately to ensure adequate sealing of the chamber.

CONCLUSION

In conclusion a brief survey is given of the properties of diffusion chambers constructed so far. In this survey the advantages and disadvantages of these chambers over the conventional expansion chambers will be indicated.

The simple diffusion chamber operating with methyl alcohol and air at atmospheric pressure is a reliable device which has many general uses. In particular, it is ideal as a demonstration apparatus since the tracks persist for a longer time in it than in an expansion chamber.

Diffusion chambers have no moving parts and can therefore be adapted more easily for operation at high pressures. Unfortunately with the heavier gases the large number of background ions stop the chamber from operating at pressures of the order of a few atmospheres. With hydrogen and helium, however, the chamber can be operated satisfactorily with pressures of the order of 20 atmospheres. Diffusion chambers thus offer a distinct advantage over expansion chambers in experiments requiring high concentrations of protons or alpha-particles.

It has been pointed out that the chamber will only operate with a limited continuous input of ionizing radiation. The chamber can, however, cope with fairly heavy ionization pulses. The cycling time of the diffusion chamber for pulsed operation can be made appreciably shorter than that of expansion chambers. Thus for air at atmospheric pressure and with pulses producing dense ionization, a diffusion chamber can be cycled about ten times faster than an expansion chamber of comparable size. This decrease in operating time may not be important when the large amount of time spent in analysing the tracks is taken into account. If a diffusion chamber is used in conjunction with a particle accelerator, however, then valuable running time of the machine may be saved.

The application of a magnetic field to a diffusion chamber with a pair of Helmholtz coils, offers no particular difficulty. For the application of a large field with iron cored magnets, the increased vertical dimensions of the chamber is a disadvantage.

A difficulty is encountered with diffusion chambers when any kind of foil is put into it. As the foil keeps the vapour just saturated at its surface, it is surrounded by a dead space which is insensitive to tracks. The resulting breaks in a track on either side of the foil are of considerable disadvantage. The dead space can perhaps be decreased by careful temperature control of the foil, but it is unlikely that it will compare favourably with that in an expansion chamber.

It has been pointed out that due to the heating effect of the drops, the sensitive depth of the chamber cannot be increased without impairing the track quality. Thus with air the limit to the sensitive depth with reasonable track quality seems to be of the order of 3 inches. This depth is adequate for measurements on horizontal beams of ionizing particles. For vertical cosmi rays, however, the resulting track length is inconveniently short. It therefore seems as if diffusion chambers will only have limited application to cosmic ray research.

With reasonable care, very sharp tracks can be obtained in a diffusion chamber. These tracks are free from the distortions that may arise on expansion in a Wilson cloud chamber. The background electron tracks always present in the chamber may, however, be of considerable disadvantage for some applications.

It was not found possible to use the diffusion chamber in the actual study of the condensation process, as the supersaturation in the chamber could not be readily controlled or measured. Usually the condensation on the large number of background ions keep the supersaturation in the chamber below the value where appreciable condensation occurs on molecular aggregates of the vapour. Even under the most favourable conditions, only a limited number of drops will be formed on these aggregates, since the condensation again maintains the supersaturation at a relatively low value.

The properties of diffusion chambers outlined above must be taken into account when planning to use such a chamber for a particular experiment. At present the diffusion technique suffers from certain limitations which make it unsuitable for more general use. Even at its present stage of development, however, the diffusion chamber offers distinct advantages over the expansion chamber for certain experiments.

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