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FINAL REPORT

Prof. Tomlinson Fort of the University of Georgia and Dr. Alfred Hind were engaged on this project from March 1, 1952 to August 31, 1952. Prof. Fort was director of the research and Dr. Hind was his assistant. Prof. Fort alone has been engaged on this project from Sept. 1, 1952 to Feb. 28, 1953.

Two papers have been made ready for publication. The first is entitled:

'The Loaded Vibrating Net and Resulting Boundary-value Problems for a Partial Difference Equation of the Second Order.'

This paper is under the authorship of Tomlinson Fort. Two copies were sent to the Office of Ordnance Research at Duke University early in December 1952, and permission asked to submit the paper for publication in Proceedings of London Mathematical Society.

The second paper is under the authorship of Alfred Hind. It bears essentially the following title:

'Convergence of approximate solutions of the vibrating membrane equation to its exact solutions.'

Two copies have been sent to the Office of Ordnance Research at Duke University and permission asked to submit the paper to the Proceedings of the American Mathematical Society.

Brief abstracts only will be given of these two papers, inasmuch as the complete papers are in the hands of the Office of Ordnance Research at Duke University. These abstracts will be followed by an equally brief resume of work completed but not yet readied for publication. It is believed that there is ample material for at least one additional paper. Certain other scattered results have been obtained and many leads followed which have not been productive. This should be helpful in further research in this field.

Abstract of Paper Number One

Let there be given a rectangular net composed of elastic cords and loaded at the points (i,j) with particles of mass m_{ij} moving with small vibrations in lines perpendicular to the plane of the net when at rest. An attempt to determine the displacement of each particle at time t, leads to a set of linear differential equations of the second order. An attempt to solve these leads one to a consideration of the difference equation

$$(1)\qquad \Delta_i\left\{b(i-1,j)\Delta_i y(i-1,j)\right\} + \Delta_j\left\{k(i,j-1)\Delta_j y(i,j-1)\right\} + \ell y(i,j) = 0$$

subject to appropriate boundary conditions. These are taken to be

$$(2)\qquad y(0,j) = y(m+1,j) = y(i,0) = y(i,n+1) = 0$$

$$i = 1, \ldots, m, \qquad j = 1, 2, \ldots, n.$$

This is tantamount to assuming the displacement of boundary particles to be zero. The consideration of the above as a characteristic-value problem is the purpose of the present paper. The characteristic determinant is the determinant of the coefficients of the linear algebraic equations obtained by substituting the points (i,j) and boundary conditions in equation (1). It is proved that the characteristic determinant is symmetrical about its principal diagonal, that all its roots are real and positive, although some may be multiple, as has been shown by examples. The work is carried forward by a kinematical method. Among other things it is proved that there are always at least m+n-1 distinct roots of the characteristic equation. These roots are denoted of $\lambda_0, \ldots, \lambda_{m+n-1}$. When $\lambda = \lambda_i$ a certain characteristic function which is denoted by V(i,j) has at least i nodal lines on the rectangular lattice.

Abstract of paper no. 2

Courant, Friedrichs and Lewy have shown that under appropriate boundary conditions a solution of

$$(3) \qquad \Delta_t \frac{u(x,y,t-\Delta t)}{(\Delta t)^2} = \frac{1}{2}\left\{\frac{\Delta^2 u(x-\Delta x,\ y,\ t)}{(\Delta x)^2}\right.$$

$$\left. + \frac{\Delta_y^2\, u(x,y-\Delta y,\ t}{(\Delta y)^2}\right]$$

with a mesh ratio of $r_1 = r_2 = 1$ will converge to a solution of the corresponding differential equation.

Lautert and Obrien proved the convergence of solutions of the equation

$$\frac{\Delta_t^2 u(x,\ t-\Delta t)}{(\Delta t)^2} = b^2\left[\frac{\Delta_x^2\ u(x-\Delta x,\ t)}{(\Delta x)^2}\right]$$

$b^2 > 0.$

to the corresponding solutions of the analagous differential equation.

The present paper treats equation (3) with $\frac{1}{2}$ replaced by $b^2 > 0$. The method is much more compact than that employed by Obrien and Lautert in their one dimensional problem and permits of immediate extension to the wave equation in n-dimensions. It is proved that for any mesh ratio $r_1 = r_2 = r$ a solution of the difference equation approaches the corresponding solution of the differential equation.

Third topic of research not yet submitted for publication.

This work has been concerned with the equation

$$\Delta_i^2 y(i-1,\ j) = \frac{S(j)}{T(i)}\ \Delta_j^2\ y(i,\ j-1)$$

subject to the condition that firstly, y be zero on the boundary of a square lying in the first quadrant and, secondly, that y be zero along the boundary of a neoquadrant of a circle. The method of attack has been to assume a solution in the form I(i) J(j). It is then proved that any solution of the problem over the square is a linear combination of products of solutions of the one dimensional Sturm-Lionville problem. It follows that all characteristic values are positive. It is proved that no characteristic value is of multiplicity greater than n .

It is proved in general that solutions exist for the neo-quadrantal problem. However, no solution can be written in the form I(i) J(j) where I and J are Sturm-Lionville functions in one-dimension.

OFFICE OF NAVAL RESEARCH

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Final Report

THEORETICAL CLOUD PHYSICS STUDIES

By

James E. McDonald

Department of Physics

Iowa State College

Ames, Iowa

January 31, 1953

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I. Homogeneous Nucleation of Supercooled Water Drops

Abstract --The experimentally observed crystallization of supercooled water near -40C is examined in terms of the theory of homogeneous nucleation. The thermodynamic and molecular-kinetic nature of the nucleation process is outlined in order to show why supercooling in natural clouds can occur so frequently. Past efforts to explain the -40C transition are examined critically and are found to contain a number of significant errors. Because the theoretical nucleation rates are extremely sensitive to the numerical value of the specific surface free energy of a water-ice interface, particular attention is devoted to the refinement of previous estimates of this parameter. It is shown that both Krastanow's and Mason's estimates were inaccurate, and that in the latter's approach, neglect of the distortion energy of the surface layer of ice led to a marked underestimate of the nucleation efficiency which was concealed by the effects of several counteracting errors. Difficulties lying in the way of a direct calculation of the distortion energy for ice are examined and found to be very serious. A crude correction for distortion effects leads to a theoretically predicted temperature of -26C for the threshold of spontaneous nucleation of drops of cloud-particle size. It is concluded that although this result lies well above the experimentally observed range of transition temperatures, it is close enough to that range, considering the inherent difficulty of assessing the effect of distortion, to strengthen the belief that the -40C transition is due to homogeneous nucleation. The implications of this conclusion for the theory of the aircraft icing process are pointed out briefly.

1. Introduction

Although a number of years have elapsed since the first clear recognition (Cwilong, 1945; Schaefer, 1946) that there exists a temperature near -40C at which ice crystals seem to form abundantly and spontaneously in a cloud of supercooled water drops, the exact physical nature of the transition has not yet been ascertained. Its importance to the subjects of cloud physics and aircraft icing makes it desirable to investigate all possible mechanisms which might account for the phenomenon. The principal division of present opinion seems to hinge upon the question of whether the observed formation of ice crystals near -40C occurs as a result of direct sublimation from the vapor phase (Cwilong, 1947; Bradley, 1951; Schaefer, 1952) or as a result of spontaneous freezing of supercooled water drops (Fisher, Hollomon, and Turnbull, 1949; Lafargue, 1950; Mason, 1952).

The sublimational hypothesis encounters serious difficulties on both theoretical and experimental grounds. First, Krastanow (1941) has shown thermodynamically that water vapor at temperatures below 0C will condense to the supercooled liquid state in an energetically easier manner than it will sublime to the solid state, since the liquid-vapor interfacial energy is certainly smaller than the solid-vapor interfacial energy in the temperature range of meteorological interest. Second, it has been found experimentally (e.g., Schaefer, 1952) that the ice phase does not make its appearance in vapor saturated just with respect to ice, but rather in vapor saturated with respect to liquid water, which implies that formation of ice crystals in the atmosphere proceeds by some intermediate process involving supercooled liquid drops (assuming no foreign nuclei to be present). A very complete and critical summary of past studies of this problem has been given by Mason and Ludlam (1951), so the background of the problem need not be elaborated here.

When one next inquires as to how a supercooled drop of water might freeze, two distinct classes of processes must be considered. If the crystallization takes place in entirely pure water, it is said to depend upon "homogeneous nucleation". If the crystallization instead depends critically upon the presence of trace quantities of some foreign substances, it is said to involve "heterogeneous nucleation". It has been clearly demonstrated within the past few years that a large number of inorganic salts will promote heterogeneous nucleation when added to suitably supercooled clouds, and much effort has been directed towards gaining an understanding of the exact mechanisms involved. In contrast to these experiments, the experiments on the -40C transition[1] seem to indicate that heterogeneous nucleation is not involved in this phenomenon; so it becomes very desirable to exploit all available experimental and theoretical methods for gaining insight into the problem of homogeneous nucleation of supercooled water. The present paper summarizes a theoretical study of this latter phenomenon.

It may be noted at the start that the theoretical expression describing the rate of homogeneous nucleation is of such mathematical form as to be extremely sensitive to the numerical values assigned to certain parameters entering into it. Consequently a major objective of the present study has been the careful examination of all quantities affecting the nucleation rate, particular effort being devoted to refining such numerical estimates of these quantities as have been made in the past. In addition, several thermodynamic aspects of the nucleation problem have been investigated and shown to be in need of revision. After all recognized refinements have been discussed here, calculations of the nucleation rate will be carried out on the basis of three independent and disparate estimates of the critically important surface free energy for a water-ice interface.

2. Theory of homogeneous nucleation

One of the principal benefits to be derived from even a qualitative study of the theory of homogeneous nucleation of supercooled liquids is an appreciation of the fact that as the temperature of a pure liquid substance is lowered to and then below the melting point of that substance's solid phase, a certain degree of supercooling is not only possible, but is in fact difficult to avoid. Thus the well-known and meteorologically important phenomenon of supercooling of cloud drops ought not be regarded by meteorolo-

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[1] Different investigators have observed the transition in question at slightly different temperatures lying within the range from about -38C to about -41C. Here, for brevity, it will be referred to simply as the "-40C transition".

gists as a paradox demanding some special explanation. Viewed in the light of the theory of homogeneous nucleation, this phenomenon is seen to be thermodynamically and kinetically inevitable in pure water drops. That it would really be the opposite case of "well-behaved" freezing at OC which would demand special explanation if invariably observed in the atmosphere does not appear to be widely appreciated, if one is to judge from comments on the phenomenon of supercooling to be found in many meteorology texts. Therefore it may be in order here to discuss briefly the qualitative nature of this problem before turning to a quantitative examination.

The supercooling of a pure liquid is quite closely analogous to the supersaturation of a pure vapor. Since the latter is of conceptual interest in cloud physics, but particularly since certain quantitative aspects of the latter are likely to be better known to most readers, the basic physical nature of homogeneous nucleation will be described first in terms of processes occurring in a supersaturated vapor.

In this latter case, one observes that a vapor which contains no intermixed foreign particles and which is not in contact with a liquid water surface of any kind may be cooled far below its nominal dew point without any appearance of water drops. The fundamental reason for this possibility of supersaturation of pure vapor is that the only way in which liquid drops can be formed under such homogeneous conditions is for a chance succession of collisions to build up embryonic water droplets one molecule at a time. But this mode of formation of drops is inherently improbable, even at temperatures well below the nominal dew point of the vapor because (to describe it in simplified terms) the total binding force exerted by very small aggregates of molecules upon one of their surface members is too low to overcome the disgregative action of thermal motions of the individual members.[2] Only by cooling the system far below its nominal dew point can one suppress this thermal disgregating effect on randomly forming embryos sufficiently to permit the embryos to gain member molecules faster by bombardment from the vapor phase than the embryos lose them to the vapor phase by evaporation. Even from as crude a model as this, one can sense that for any given temperature below the nominal dew point there ought to exist a critical embryo radius below which an embryo is unstable and will tend to evaporate, but above which it will tend to grow rapidly. Furthermore, the same model suggests the important relation that the magnitude of this critical radius must surely decrease with decreasing temperature. Both of these conclusions can be given firm support and, still better, quantitative expression by means of the corresponding thermodynamic arguments.

One of the main results of the thermodynamic argument is a quite familiar relation, Kelvin's equation. However, the form into which this equation is almost invariably put in meteorological applications, and the corresponding way in which it is interpreted, tend to conceal its interesting implications as an equation from the theory of homogeneous nucleation. Kelvin's equation, as conventionally written, relates the vapor tension e_r of a pure water drop of radius r and temperature T to the vapor tension e of a plane

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[2] For aggregates containing, say, only a half dozen molecules, the binding force for any given member molecule may be understood in terms of the small total number of other molecules available to attract the given molecule. For larger aggregates, the total number of members ceases to be the significant parameter, since it is well established that the range of intermolecular forces is so small as to become generally negligible over distances of the order of two or three molecular diameters. Instead, the deficiency in binding energy for a surface molecule in an aggregate of, say, a few hundred molecules depends almost entirely on a purely geometric effect due to the large surface curvature of such tiny aggregates. The curving surface of the embryo falls away so rapidly on all sides of a given surface molecule that there exists a slight deficit of near-neighbors whose radially inward components of attraction go to make up a portion of the total binding force in a perfectly plane liquid surface.

surface of pure water of density ρ_ℓ, specific surface free energy (surface tension) σ_ℓ, and temperature T, according to

$$\ln \frac{e_r}{e} = \frac{2\sigma_\ell}{\rho_\ell R' T r} \qquad (1)$$

where R' is the gas constant per gram for water vapor. It is usually, and correctly, stated that Kelvin's equation shows how much larger the vapor tension of a tiny drop is than that of a plane surface of the same liquid at the same temperature. What is too frequently ignored in meteorological discussions, is that the same equation is equally appropriately regarded as an equation giving the critical embryo radius as a function of the degree of supersaturation and hence of the degree of undercooling below the nominal dewpoint. To bring out the latter interpretation, one may substitute for $\ln(e_r/e)$ from the integrated form of Clapeyron's equation to get, on expressing it as an equation to determine r,

$$r = \frac{2\sigma_\ell \overline{T_0}}{\rho_\ell L_v (T_0 - T)} \qquad (2)$$

where L_v is the latent heat of vaporization of the liquid and T_0 is the temperature (greater than T) at which e_r corresponds to the saturation vapor pressure, i.e., T_0 is simply the nominal dew point of the given sample of supersaturated vapor which is in equilibrium with drops of radius r. Equation (2), though still essentially Kelvin's equation, tells rather more than (1), for it defines the radius r that an embryo must just attain to grow rather than to evaporate in the presence of water vapor which has been undercooled isobarically from its nominal dew point T_0 to its actual temperature T. Kelvin's familiar but amazing derivation of (1) from consideration of a capillary column (Humphreys, 1940) completely conceals this physical interpretation. A more straightforward thermodynamic derivation brings it out clearly since r in (1) or (2) is then seen to represent the radius for which the net free energy change due to addition of molecules to an embryo attains a maximum. For embryos smaller than this critical size, the free energy increase due to increase of surface area accompanying the addition of more molecules more than cancels the free energy decrease accompanying the phase change. Hence in this r-range, further growth does not tend to occur "spontaneously" in the thermodynamic sense, i.e., the process does not involve a net decrease of free energy. For embryos greater than the critical size, the r^2 dependence of the surface term is overpowered by the r^3 dependence of the bulk term and rapid growth ensues spontaneously. Viewed in this light, the critical radius given by (2) is that for which the free energy has a stationary value.

To gain a firmer feeling for the homogeneous nucleation process as it operates in the case of supersaturated vapor, one may use (2) to compute the actual size of these critical embryos in a particular case. Thus, a sample of water vapor which has a vapor pressure of 17 mbs is known to be nominally saturated at 15C. If cooled isobarically to 5C in the absence of condensation nuclei and free water surfaces, it attains a relative humidity of about 200 per cent, and (2) reveals that homogeneous nucleation cannot then occur unless chance collisions build up embryos with radii of about 17 Angstrom units. Since this radius is of the order of ten times the molecular radius of water, it follows that spontaneous condensation will not begin unless aggregates of some 10^3 water molecules are built up. This turns out to be so very improbable at the vapor density and temperature in question that the chance of even one such critical embryo appearing in a volume of many liters of vapor in a time of many minutes is negligible.

The preceding discussion of homogeneous nucleation in a supersaturated vapor raises the question of how one predicts the average rate at which embryos of the critical size may form by random molecular processes at a given degree of undercooling. This question is of equal significance in the problem under discussion in this paper, namely nucleation of a supercooled liquid; so, having outlined the basic features of a typical homogeneous nucleation process, attention will now be returned to this problem of primary interest here. Just as was true for the case of nucleation of vapor, one can only expect to find embryos (now crystalline embryos) forming in a supercooled liquid as a result of random collision processes; and, again, survival of these is prejudiced by chance until they can grow to such size that the surface molecules in the embryonic crystal lattice are bound with energies rather greater than the average thermal vibrational energy corresponding to the temperature of the liquid. An equation very similar to (2), namely (5) below, specifies the critical crystallite radius for any given degree of supercooling, and the problem is to find a theoretical expression for the rate of formation of these critical embryos per unit volume of supercooled liquid as a function of the degree of supercooling.

This problem has been solved through the successive efforts of Becker and Döring (1935), Turnbull and Fisher (1949), and others. An extensive discussion of the nucleation rate problem (exclusive of the recent and important contribution of Turnbull and Fisher) may be found in Frenkel (1946); and a more recent summary has been given by Bradley (1951). In a liquid supercooled below its nominal freezing point T_o to an actual temperature T, the rate of formation of nuclei (critical embryos) per unit volume per unit time is given by Turnbull and Fisher as

$$J \approx \frac{nkT}{h} e^{-\left(\frac{A+F_c}{kT}\right)} \tag{3}$$

where J is the specified nucleation rate, n is the number of molecules per unit volume in the liquid phase, k is Boltzmann's constant, h is Planck's constant, A is the free energy of activation for self-diffusion of the liquid molecules, and F_c is the free energy of formation of a nucleus. The contribution to this theoretical equation made by Turnbull and Fisher was the approximate evaluation of the prefactor of the exponential in (3) based on the quantum statistical theory of absolute reaction rates (Glasstone, Laidler, and Eyring, 1941). It is to be noted that nkT/h is not simply the collision frequency, as was once thought to be true. Very loosely, (3) may be said to give J as the product of a fundamental molecular (or atomic) rate constant, nkT/h, multiplied by two fractional probability factors rather similar to Boltzmann factors. The first, exp(-A/kT), cuts down the fundamental rate by a fraction measuring the rather low probability that any given liquid molecule will possess at any given instant sufficient energy to permit it to "break loose" from the liquid structure and reach an energy state in which it is free to diffuse from the liquid region onto and into the embryonic lattice (see Section 9 below). The second factor, exp($-F_c/kT$), further reduces J by a factor which measures the generally very small probability that random processes can succeed in amassing an embryo of critical size in the face of the associated free energy increase of the system. Clearly, homogeneous nucleation should be thought of as an intrinsically improbable event, as has been stressed above in pointing out that the common occurrence of supercooled cloud drops is not really paradoxical at all.

The activation energy for self-diffusion, A, cannot readily be expressed as a thermodynamic function of more elementary parameters, so its evaluation will be reserved for Section 9. On the other hand, the free energy increase, F_c, associated with the formation of an embryo of critical radius r_c (or of characteristic length r_c if one visualizes formation of some other geometric shape than a sphere) is found from thermodynamic considerations (see, for example, Frenkel, 1946) to be

$$F_c = \frac{1}{3} \sigma_s g r_c^2 \tag{4}$$

where σ_s is the specific surface free energy of the solid-liquid interface and g is a geometric factor such that $g r_c^2$ is the total surface area of the critical embryo. An expression of the form of (4) holds so long as edge energies may be ignored. The critical radius, r_c, is given by an equation analogous to the Kelvin equation written above as (2) for the corresponding case of vapor-liquid nucleation. The form of the r_c-equation given by Frenkel (1946) is

$$r_c = \frac{2\sigma_s T_0}{\rho_s L_f (T_0 - T)} \qquad (5)$$

where ρ_s is the density of the solid phase and L_f is the latent heat of fusion of the substance in question. It has been argued qualitatively in the discussion of vapor nucleation above that the rate of formation of nuclei (critical embryos) increases with increasing degree of supercooling. Superficial inspection of (3) might seem to yield a contradiction to this, for the nkT/h prefactor as well as the factor kT in the exponent both tend to lower the nucleation rate as the temperature of the supercooled liquid falls. It is, however, in spite of these factors and because of the sensitive dependence of F_c on T, as given by (4) and (5), that J increases rapidly with decreasing temperature. Hence spontaneous crystallization does tend to become more probable the greater the degree of supercooling. The problem of cloud physical interest is: Does this probability pass through some sort of threshold value near -40C such that freezing of drops becomes nearly inevitable within periods of time characteristic of cloud processes? Some past efforts to answer this question will be examined next.

3. Previous cloud physical applications of nucleation theory

The present position of the theoretical investigation of homogeneous nucleation of supercooled water will be summarized in this section by reviewing the salient features of the principal past studies of this problem. In the course of the present study, significant errors have been found in each of these. Perhaps the major contribution of the present investigation has been the detection of and at least partial correction for these errors.

Krastanow (1941) sought to apply the theoretical work of Becker and Döring (1935) and of Volmer (1939) to the meteorological problems of homogeneous and heterogeneous nucleation of both supersaturated vapor and supercooled water. Although he reached conclusions (e.g., energetically greater probability of condensation than sublimation in vapor below 0C) whose significance have not always received the attention they seem to deserve, he could make no definitive calculations because at the time of his writing the rate-factor appearing in (3) had not yet been adequately evaluated. Krastanov made certain estimates of A and of σ_s which will be discussed below. It appears not to have been previously noticed that Krastanow failed to take account of the appreciable temperature variation of the latent heat of fusion of water (see Section 5 below) in his calculations of σ_s .

Fisher, Hollomon, and Turnbull (1949), recognizing that it is very difficult to determine σ_s by experiment or theoretical calculation, used nucleation theory to work backwards from the observed -40C transition temperature to <u>compute</u> σ_s on the assumption that -40C is in fact the temperature for which J becomes of the order of unity. For unstated reasons, they omitted A in the nucleation equation which, as will be pointed out below (Section 9), is neither qualitatively nor quantitatively permissible. Second, they, like Krastanow, ignored the substantial decrease of L_f with decreasing temperature. Finally, although they did not state explicitly what mass of supercooled water they were considering, one can determine this by solving for their N (the n of the present paper multiplied by the volume considered) after putting their computed value of σ_s , 32.8 erg cm^{-2}, back into their equation along with all other numerical values they specify. One finds in this way that they were tacitly considering the -40C (-38C according to them) transition as occurring when one nucleus formed each second somewhere within a sample of one <u>gram</u> of supercooled water. This was a quite fallacious basis for the calculation since the temperature at which homogeneous nucleation occurs will clearly vary with the mass of liquid involved, and experimental observations yielding the -40C effect concern individual water drops whose masses are only of the order of 10^{-9} gm. Because of these several errors, no significance can be attributed to their estimate of σ_S. A corrected calculation of the same type will be made below at the end of Section 10.

Lafargue (1950) made a rather curious calculation whose results he presented as proof that the -40C transition is due to homogeneous nucleation of supercooled drops. He began by pointing out that x-ray diffraction studies of the structure of liquid water have revealed that each oxygen is surrounded tetrahedrally by four other nearest-neighbor oxygens at 2.76 Angstroms and that the second-nearest neighbors, twelve in number, lie at a radial distance of 4.53 Angstroms. Next, and without further comment, he inserted r_c = 4.53 Angstroms into the Gibbs-Thomson equation (5) along with numerical values for all quantities appearing therein except T, and solved for T. His result was -41C, in excellent numerical agreement with Cwilong's (1947) observed value for the transition point. He concluded that this argument had demonstrated that the transition must be dependent upon homogeneous nucleation. For several reasons this argument of Lafargue's cannot be accepted. First, although the fact that the radius of the second sphere of coordination in liquid water is about 4.5 Angstroms is well established, there is no good a priori reason why one should insert this particular distance rather than, say the first or the third, or even some higher order coordination radius into the Gibbs-Thomson equation as an alleged critical radius. It is an essential feature of the homogeneous nucleation process that r_c is not a constant, as this step of Lafargue's assumes, but is instead a quantity which decreases with decreasing temperature. Second, for Lafargue to have sought an explanation of the -40C transition in terms of an essentially static model rather than to grapple with the critically important notion of the rate of nucleation was to ignore the intrinsically kinetic nature of the nucleation process, namely that at all times there exists a spectrum of rates of change formation of embryos of various sizes from two molecules on up, and that spontaneous crystallization only occurs when the rate of formation of embryos of critical size becomes of the order of one per volume unit and time unit characteristic of the experiment. Lafargue was effectively saying that the ice-like short-range order in supercooled water waits passively for the temperature to fall far enough for the local structure to simulate an ice embryo of size sufficient to satisfy the Gibbs-Thomson relation. This view ignores the fundamental role played by statistical fluctuations in the nucleation process. Third, Lafargue used the value of L_f corresponding to 0C in a calculation referring to -41C. Had he used the value of L_f appropriate to -41C (see Section 5) with all other variables unchanged, he would have found a transition temperature of -58C instead of -41C, and the agreement with observation would have disappeared. It would seem to follow from these objections, unfortunately, that the problem of explaining the -40C transition was certainly not solved by Lafargue.

A valuable x-ray diffraction study of the molecular structure of supercooled water (Dorsch and Boyd, 1951), which appears to have been stimulated in part by Lafargue's paper, revealed that the peak in the angular intensity pattern for water at a scattering angle of 18 degrees becomes increasingly better resolved as the degree of supercooling increases down to those investigators' lower limit of observation of -16C. Since this peak is due to x-ray scattering by the second sphere of coordination at about 4.5 Angstrom radius, Dorsch and Boyd concluded that the structure of water does grow increasingly ice-like as supercooling proceeds, as suggested a number of years ago by Bernal and Fowler (1933). They pointed out that this trend suggests that at the still greater degree of supercooling prevailing near the -40C point, the structure of liquid water might be so nearly isomorphic with ice as to justify Lafargue's disregard of the whole concept of the work of formation of an ice embryo. However, the work of formation (properly the free energy of formation) of a nucleus goes to zero, according to (4) only if σ_S goes to zero; and if isomorphism developed to this extent near -40C, then Lafargue's calculation would become invalid for still another reason, since his result requires a value of 10.5 erg cm^{-2} for σ_S . There seems no way to justify Lafargue's approach.

A still more recent effort to account for the -40C transition in terms of homogeneous nucleation is due to Mason (1952). Unlike Krastanow who did not have available the quantum-statistical expression for the rate factor in the nucleation equation, and unlike Lafargue who may have been unaware of it, Mason proceeded from Turnbull and Fisher's equation, (3) above. Finally, unlike Fisher, Hollomon, and Turnbull, he did not merely use the equation to make an estimate of σ_S by reasoning backward from the observed -40C transition temperature assuming the very thing which the meteorologist seeks to confirm. Instead, Mason made a direct attack on the problem by estimating σ_S on theoretical grounds, and then used this estimated value in (3) to study the behavior of J.

In several of the following sections, a number of refinements of detail in Mason's treatment will be discussed. Here only one general objection must be raised to the basis upon which Mason sought to demonstrate agreement between theory and observation. Aware of the inherent uncertainty in his theoretical estimate of σ_S , Mason found that values of $\frac{\partial(\log_{10} J)}{\partial T}$ were less sensitive to uncertainties in σ_S than were values of $\log_{10} J$ itself and so he only discussed the former in his paper. On calculating the values of that derivative near -40C, he found a nearly ten-fold increase in J per Centigrade degree in that vicinity, and he offered the rapidity of this increase, *per se*, as the explanation of the experimental observations of a sudden transition of supercooled clouds in the neighborhood of -40C.

Now a rapid temperature variation in the nucleation rate near -40C is certainly necessary to any statistical explanation of the observations, but it is not by itself sufficient. One must ask whether the nucleation rate might not vary just as rapidly at some temperatures other than -40C; and equation (3) yields the answer that it does. Indeed, near -30C the rate of formation of nuclei is found, from (3) using Mason's figures, to change by a factor much greater, 250 per degree; and at -20C it changes by a factor of one hundred million per degree! Hence the mere ten-fold change per degree near -40C can certainly not *by itself* be regarded as implying that the neighborhood of -40C will be a preferred region for transition. Consequently, it becomes logically indispensable to consider not just the steepness of the temperature variation in the nucleation rate, but also the absolute values of that rate.

By taking this latter approach, an explanation for the observed phenomena might have been presented in a rather more convincing form than that chosen by Mason. A further important modification in approach should then have been to evaluate the nucleation rates not simply in terms of nuclei per cubic centimeter per second but rather in terms of nuclei per drop per second.[3] The latter is the pertinent rate here since each drop is essentially an isolated physical system in the process in question, and if a given drop is to crystallize within a reasonable length of time, t, there must be a high probability of at least one nucleus forming somewhere within that drop during the time t. Failure on the part of Fisher, Hollomon, and Turnbull (1949) to look at the -40C problem in this manner has already been cited. A measure of

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[3] Mason has pointed out (private communication) that his original approach was exactly this one, but that his recognition of the difference in sensitivity to σ_S of J and of $\partial J/\partial T$ led him to discuss only the temperature derivatives. In so doing he apparently overlooked the fallacy of this approach occasioned by the even steeper J-variations at temperatures warmer than -40C. And, indeed, a merely large value of $\partial J/\partial T$ occurs at -40C for almost any halfway plausible numerical values one may insert into (3).

the average time between nucleation events within each drop is given by the reciprocal of the nucleation rate per drop. Using the several tentative numerical values suggested by Mason for the parameters entering into (3), one finds for this "average nucleation time" the values shown in Table 1 for drops of 1, 5, and 10 micron radii. It is in considering the absolute values of these tabulated times as well as their rapid temperature variation that one finds quite nice apparent agreement between observation and Mason's work.

Table 1. Average time between nucleation events within water drops of radius r at various temperatures. Revised from Mason (1952).

Temperature	r = 1 micron	r = 5 microns	r = 10 microns
-36C	187 days	32 hours	4.5 hours
-37	6.9 days	80 minutes	10 minutes
-38	11 hours	5 minutes	40 seconds
-39	42 minutes	20 seconds	2.5 seconds
-40	5 minutes	2 seconds	0.3 seconds
-41	30 seconds	0.2 seconds	0.03 seconds

In experiments where the supercooling is produced in an adiabatic expansion, the entire nucleation process must occur in times of the order of seconds (unless the chamber is unusually well insulated). Hence the times shown in Table 1 suggest that no crystals should be observed in a cloud of drops whose radii are of the order of microns until the peak expansional cooling extends down to near -40C, but that near that point the probability of nucleation finally rises to a level at which every drop in the 5 - 10 micron range may be expected to experience a nucleation event within the sensitive time of the chamber. In a natural cloud where the period during which a given drop exists at a given temperature is of the order of minutes, one would expect, from the implications of Table 1 that spontaneous freezing could occur at a higher temperature, but only a degree or two higher because of the extreme temperature sensitivity of nucleation. Thus, to emphasize the basic issue here, the apparent success of a statistical theory of homogeneous nucleation is to be assessed not just on the basis of its prediction of a rather steep ascent of the nucleation probability per drop in the -40C region, as Mason tacitly suggested, but much more on the basis of whether it predicts that this ascent will in fact carry that probability to values implying that a majority of drops will be nucleated at least once in the time interval characteristic of the cooling process involved.[4]

Judged on both these grounds, the version of Mason's work shown in Table 1 looks nearly perfect. Even the slight spread of the experimentally observed transition temperatures is readily understood in terms of Table 1 if different observers worked with clouds of slightly different drop-size distributions, and particularly if the sensitive times of their chambers varied from fractions of a second to several seconds. Both types of dispersion in experimental conditions are entirely plausible. The writer's first interest in nucleation theory was aroused by these implications of Table 1. It is with some regret, then, that he must next point out that an extensive study of the basis of Mason's calculations has uncovered a number of defects which, when removed in the best way recognized by the writer, destroy the neat agreement between Table 1 and the experimental observations. The next six Sections will be devoted to a critical examination of these points and to efforts to improve, in every way possible, the basis of the calculations of the dropwise nucleation rates.

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[4] The calculated rates shown in Table 1 have been given here despite their now recognized lack of validity, partly to document a logical objection to Mason's mode of assessing his results, but much more to illustrate, for the reader not familiar with nucleation theory, exactly the sort of numerical behavior of the dropwise nucleation rates which one would hope to find in searching for a statistical explanation of the -40C transition.

4. The Gibbs-Thomson equation

The theoretical nucleation rate is determined jointly by (3), (4), and (5). The writer has been unable to find any basis for modifying (3) or (4), though (4) will be incomplete if one can demonstrate that edge energies are being ignored at the expense of numerical accuracy. The Gibbs-Thomson equation, (5), however, appears to require a slight change. Mason followed Frenkel (1946, p. 415) in using the form (5); but an examination of Frenkel's derivation of this relation reveals that it is only approximately correct for such large values of $\left(T_0 - T\right)$ as one encounters in the present problem. From a thermodynamic argument which need not be reproduced here (Frenkel, 1946, p. 368), one can show that

$$(v_\ell - v_S)dp = 2\sigma_S v_S \, d(1/r)$$

where v_ℓ and v_S are the specific volumes of the liquid and solid phases respectively and p is the external pressure on the system. Eliminating $(v_\ell - v_S)$ between this equation and the <u>differential</u> form of Clapeyron's equation, and integrating between the limits $r = r_c$ at T and $r = \infty$ at $T_0 = 273K$, one gets as a more generally applicable form of the Gibbs-Thomson equation,

$$r_c = \frac{2\sigma_S}{\rho_S L_f \ln(T_0/T)} \tag{6}$$

The form (5) given by Frenkel and used by Mason is an approximation to (6) obtainable by expanding $\ln(T_0/T)$ into a series and using only the first term. For only very small degrees of supercooling, negligible error is introduced by using (5); but when as here $T_0 - T$ becomes 40 Centigrade degrees, there is about an 8 per cent error in (5), which means about a 16 per cent error in the computed value of F_c, and finally a much larger error in J. It may be well to state here that though this elimination of an error of less than 10 per cent in r_c represents a rather slight improvement when viewed against the large uncertainties which will be shown to exist in σ_S in Section 7, still it enters (6) factorially and not additively, and so the revision is meaningful. A more concrete measure of the significance of the replacement of (5) by (6) is found in the fact that, keeping all other parameters unchanged in Mason's calculations, this modification raises J by a factor of 10^4 for drops at -40C, and thereby raises the predicted "spontaneous freezing point" by about 4 Centigrade degrees, from near -40C as shown in Table 1 to about -36C. That is, the change from (5) to (6) already alters appreciably the sort of close agreement with observation which made Table 1 seem so promising an explanation of the -40C transition.

5. Latent heat of fusion of ice

It has been pointed out above that previous investigators of the problem of homogeneous nucleation of supercooled water have failed to take account of the temperature dependence of the latent heat of fusion of ice. It will next be shown that this oversight has introduced a quite large error into this previous work, including Mason's work as modified in Table 1.

A general thermodynamic relation, sometimes referred to as Kirchoff's equation (Glasstone, 1947), relates the isobaric temperature variation of the latent heat of fusion to the difference in specific heats at constant pressure for the liquid phase, c_{pl}, and the solid phase, c_{ps}, according to

$$\left(\frac{\partial L_f}{\partial T}\right)_p = c_{pl} - c_{ps} \qquad (7)$$

For water substance at 0C, $c_{pl} \approx 1$ cal gm^{-1} deg^{-1} while $c_{ps} \approx 0.5$ cal gm^{-1} deg^{-1}, so the latent heat of fusion of ice decreases with decreasing temperature at a rate of about 0.5 cal $gm^{-1} deg^{-1}$ just below the melting point. If this rate held constant down to -40C, L_f would decrease to about 60 cal gm^{-1} at that temperature. Actually the situation is slightly worse, since c_{ps} is known to decrease with decreasing temperature (Giaque and Stout, 1936), and at the same time c_{pl} increases with decreasing temperature according to experimental results extending to -15C (Scheel and Heuse, 1909) plus theoretical extrapolation to -50C (Goff, 1949) based on thermodynamic relations between c_{pl} and de/dT.

Values of $L_f(T)$ are shown in Figure 1. The dashed portion of the curve in Figure 1 below -50C is the writer's own simple <u>linear</u> extrapolation beyond Goff's values. Although this part of the curve is a gross extrapolation, it will be used in certain estimates made in Section 10. The very careful nature of Goff's extrapolation to -50C from experimental data extending to -15C warrants considerable faith in the values down to well below the -40C transition point, which is fortunate here. It is clear from Figure 1 that previous analyses of the homogeneous nucleation of supercooled water, in which a value of 80 cal gm^{-1} has repeatedly been used for L_f in the Gibbs-Thomson equation, have thereby been very seriously in error inasmuch as this roughly 40 per cent overestimate of L_f is raised to the second power and then used in an exponential. For example, if just this one correction is made in Mason's work it shifts the predicted transition point from near -40C as implied in Table 1 to the very much lower temperature of -68C. Comment has already been made on what the same type of error did to Lafargue's work. In Section 7, below, it will be shown that failure to recognize that L_f decreases with decreasing temperature produced still another type of error in Krastanow's (1949) estimate of σ_S .

There is a second, less obvious correction of L_f that must be considered. This second correction has also been overlooked in previous studies, though fortunately without numerical error since still another oversight closely compensates this one, as will be shown later. Despite this near-cancellation of one error against another, it seems advisable to examine each here to avoid possibility of one of them being detected and corrected and not also the other. The present point hinges upon the fact that the ice whose fusion is involved

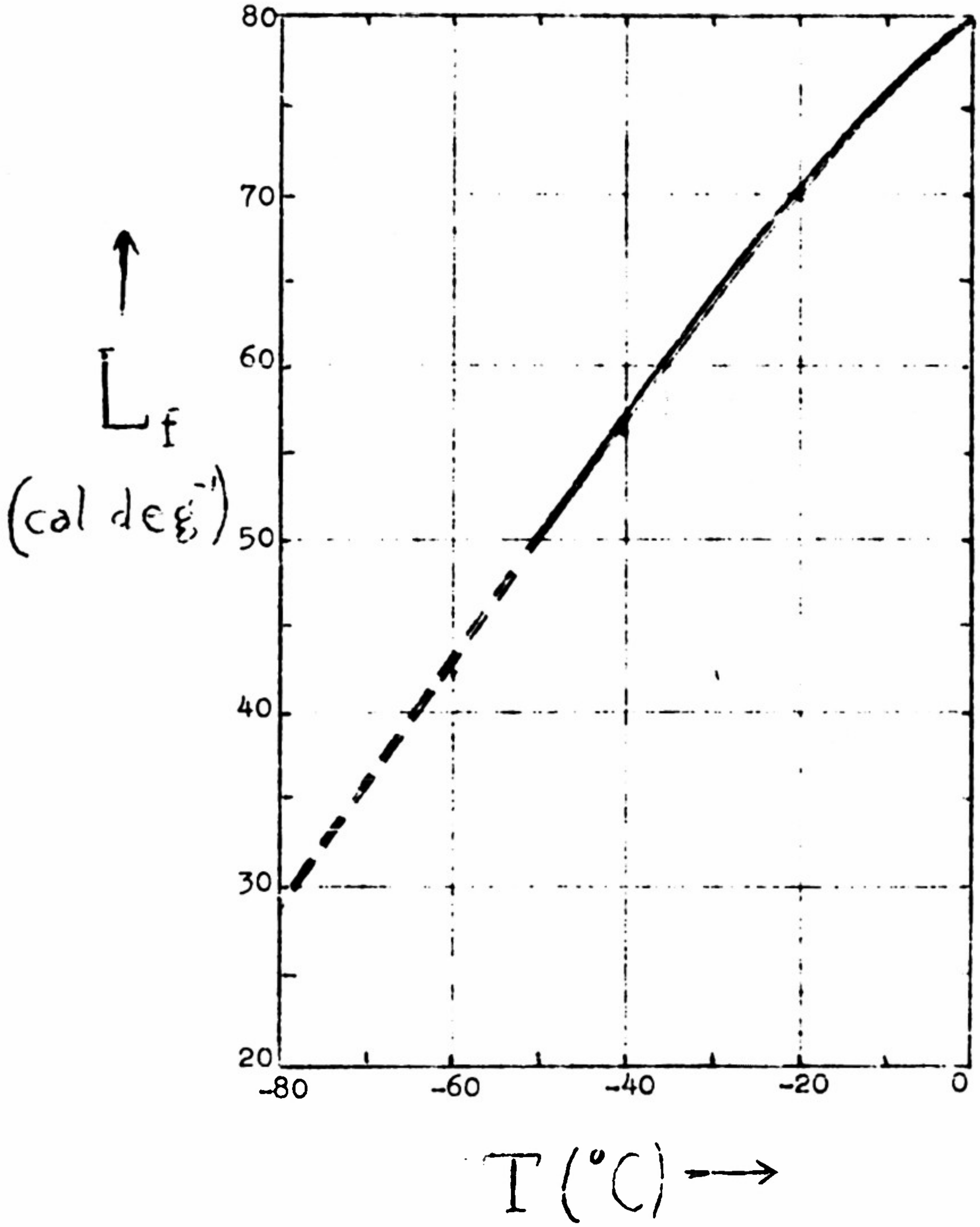

Figure 1. Temperature dependence of the latent heat of fusion of ice, L_f. Values from 0C to -50C after Goff. Values from -50C to -80C obtained by linear extrapolation.

in homogeneous nucleation occurs in the form of extremely small embryos with radii of the order of 10 - 20 Angstroms. For particles of such small radii of curvature, there appears the same sort of geometric effect on binding energy as was referred to above in a footnote in Section 2 for the case of liquid embryos. The binding energy (and hence the latent heat of fusion) must decrease with decreasing embryo radius, and although this decrease is entirely negligible for radii above, say, 10^{-6}cm, it becomes numerically significant for particles of the size of those here in question.

To obtain thermodynamically a measure of the reduction of L_f due to surface curvature effects, consider a spherical ice embryo of radius r from which a small mass dm of water molecules is removed by melting. Let L_f now denote the latent heat of fusion for $r = \infty$ at the temperature in question. Then the amount of energy dQ that must be supplied to melt off dm grams of ice from the sphere is <u>less</u> than $L_f dm$ by the amount of the decrease of surface energy, $\sigma_s\, dA$, where dA is the change in surface area of the embryo accompanying the spherically symmetric stripping of the dm grams. Thus, inasmuch as

$$dm = 4\pi \rho_s r^2 dr$$

and

$$dA = 8\pi r dr,$$

and since

$$dQ = L_f dm - \sigma_s dA,$$

it follows that

$$L_{fr} \equiv \frac{dQ}{dm} = L_f - \frac{2\sigma_s}{\rho_s r}, \qquad (8)$$

where L_{fr} is the latent heat of fusion per gram of ice at a radius of curvature r. It may be noted that σ_s itself is size dependent, but allowance for this would only introduce second-order correction into (8).

The numerical magnitude of this size correction of L_f is subject to the same relative error as is the value assigned to σ_s, so it will turn out that its precise value cannot here be determined since σ_s will finally turn out to be uncertain. However, an estimate of its effect can be made by considering a nuclear radius of 10 Angstroms (approximate size in water nucleation at -40C) and assuming $\sigma_s \approx 20$ erg cm^{-2} (rough average of three estimates of σ_s given in Section 7 below). In this case the correction term amounts to about 13 per cent of L_f. This correction is thus about half again as large as the correction due to the revision in form of the Gibbs-Thomson equation, which was shown in Section 4 to shift the theoretically predicted transition temperature by about 4C.

It is interesting to compare (8), which has been obtained here thermodynamically, with the results of an approximate molecular argument given by Benson and Shuttleworth (1951). They calculated the ratio of the molecular heat of vaporization for a small cluster of molecules to that of a plane surface on the assumption that all pairs of molecules interact according to an inverse twelfth power repulsive potential plus an inverse sixth power attractive potential. For the simplest case of a central molecule surrounded by twelve close-packed neighbors, they computed the ratio to be about 0.4. Since Benson and Shuttleworth's model implies that this ratio may be expected to vary approximately as $(1 - cN^{-1/3})$, where c is a constant and N is the number of molecules in the cluster, their value of 0.4 for thirteen molecules may be raised to about 0.6 for a cluster of the size referred to in the preceding paragraph, since such a cluster would comprise 25 to 30 water molecules. The corresponding ratio for latent heats of fusion predicted by (8) was 0.87. This order of magnitude agreement with Benson and Shuttleworth's result is surprisingly good in view of the present uncertainty in σ_s and in view of the other approximations involved in both approaches to this ratio. It seems appropriate to regard this agreement in size effect estimates as providing mutual support for these quite independent methods of estimating latent heats of small aggregates of molecules.

6. Density of ice

The coefficient of volume expansion of ice near 0C is (Dorsey, 1940) 1.5×10^{-4}deg.$^{-1}$. It follows that even at -50C thermal contraction has increased the density of ice by only about one per cent of its value of 0.92 at 0C. This change is too small to be considered here. It will, furthermore, be opposed by a decrease of density associated with surface distortion of the ice lattice (Brown, 1947). Since nuclei have relatively large surface/volume ratios, this latter type of density change may become sensible. Shuttleworth (1949) calculates that it amounts to several per cent for homopolar crystals, but this density reduction is localized almost entirely to a surface monolayer. Pending further developments in the theory of dipole-bonded crystals like ice, the effect must be ignored.

7. Surface free energy of a water-ice interface

No one has yet devised an experimental technique for directly measuring σ_s for an interface between supercooled water and ice, nor even for water and ice at the triple point, to the writer's knowledge. Nothing could be more unfortunate for the problem at hand. Inspection of (3), (4) and (6) reveals that σ_s has a controlling influence on the homogeneous nucleation rate since it enters to the third power in an exponential in the J-equation. It follows that major effort should be devoted to getting improved estimates of σ_s by any available theoretical means. In the present section, attempts will be made to refine Krastanow's (1941) and Mason's (1952) values. The present study has not led to any essentially new basis for estimating σ_s, but it has revealed that numerically significant changes have to be made in both of these existing methods.

Krastanow's basis for estimating σ_s depended upon a general relationship rather casually suggested by Volmer (1939, p. 181). The latter proposed that one might get a rough value of this quantity from the proportion

$$\frac{\sigma_s}{L_f} \approx \frac{\sigma_\ell}{L_v} \tag{9}$$

The validity of such a proportion depends on how surface free energies and latent heats are related, respectively, to intermolecular binding energies, and depends particularly on whether that relationship is identically the same for the solid and the liquid states. It must not be thought that this identity has been proved by either Volmer or Krastanow; in fact neither has given any comment of justification for (9). Since Krastanow's estimates of as derived from (9) have been used without apparent question in subsequent studies by other investigators (Lafargue, 1951; Weickmann, 1951), and will also be used below, it becomes a matter of some interest to try to assess this equation's validity, even if only to first approximation.

In the latter spirit, the writer offers the following crude derivation of Volmer's equation based upon a result of a theoretical analysis of the relation between surface energies and latent heats of sublimation of crystals (Shuttleworth, 1949). From direct molecular calculations of the surface energy, Shuttleworth found that an expression of the form $a_s^2 \sigma_s'/L_s = K$ holds for homopolar crystals, where a_s is the intermolecular (or interatomic) distance in the solid, σ_s' is the surface free energy of the solid against its vapor, and K is a constant depending upon the interatomic potential used and on the lattice geometry involved. For a (111) face in a face-centered cubic homopolar crystal, K is about 0.2 for one plausible potential. Shuttleworth discussed quantitatively the effect on σ_s' due to surface distortion of the lattice of van der Waals crystals, but could only point out qualitatively that for crystals in which permanent dipoles influence the bonding will be appreciably lower due to greater contribution of distortion energy. Since water is a substance of particularly marked dipole-dipole bonding (hydrogen bonding), one would expect a K-value somewhat below 0.2 in the case of interest here.

If one next considers the liquid state, he observes that an interaction picture very much like that assumed by Shuttleworth exists as far as concerns the short-range order important in homopolar or dipole bonding, and particularly so in the case of supercooled water, which appears to have a very ice-like structure, at least out as far as second-nearest neighbors (Dorsch and Boyd, 1951). Hence one might expect that supercooled water should also be characterized by a Shuttleworth relation of the form $a_\ell^2 \sigma_\ell / L_v \approx K'$, where a_ℓ is the intermolecular distance in the liquid structure and K' is the new constant for liquid water. But since to within the limits of accuracy of the present discussion $a_s \approx a_\ell$, and since structural similarities and interaction similarities should imply $K \approx K'$, it should follow that a proportion of the form

$$\frac{a_s^2 \sigma_s'}{L_s} \approx \frac{a_\ell^2 \sigma_\ell}{L_v} \qquad (10)$$

might hold approximately. Furthermore, each ratio in (10) would be expected, as Shuttleworth noted, to be somewhat smaller than 0.2. Actually, the right member, which is readily evaluated, equals 0.08 at 0C[5]. From the 0C value of L_s, one finds from (10) that σ_s' is about 85 erg cm^{-2}. Then invoking Antonov's rule (Adam, 1951) to estimate σ_s, one finds

$$\sigma_s \approx \sigma_s' - \sigma_\ell \approx (85 - 75)\,\text{erg cm}^{-2} = 10\ \text{erg cm}^{-2}$$

Finally, putting this estimated 0C value of σ_s back into Volmer's equation (9), one finds that the left and right members have numerical values of 2.98×10^{-9} and 3.01×10^{-9}, respectively, when the latent heats are once again expressed in ergs per gram. This agreement of the two members of (9) to better than one

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[5] One must use the latent heats per molecule in Shuttleworth's relation.

per cent is almost certainly fortuitous because of the many approximations involved in the preceding discussion. What can be said, however, is that Volmer's equation has now been provided with at least some theoretical support, which has not been true previously, to the writer's knowledge. Briefly, one can regard (10) as following from Shuttleworth's relation plus the similarity in structures of ice and supercooled water; and Volmer's equation (9) then appears to be related to (10) through Antonov's rule. It should be strongly emphasized, however, that (9) has been justified here in only a very approximate manner; so computations based upon it simply cannot yet be regarded as definitive, a point which has not been given deserved emphasis in previous applications.

Since (9) has now been rendered at least plausible as one relation for making approximate calculations of σ_s, the next step is to examine whether Krastanow's (1941) applications of (9) can merely be taken over here for later use in estimating J. Although Krastanow did not state the numerical values he used to compute his σ_s values, the writer finds that Krastanow's results can be reproduced to within one per cent by introducing into (9) temperature-dependent values of σ_ℓ extrapolated below 0C from data such as those given by Zemansky (1943) and temperature-dependent values of L_v (List, 1951), but by using a constant value of L_f equal to 80 cal gm^{-1}. This last feature of Krastanow's approach was erroneous because of the temperature dependence of L_f. His original computed values of σ_s are shown in the first line of Table 2. By using L_f values taken from Figure 1, one obtains the set of values shown in the second line of Table 2.

Table 2. Water-ice interfacial free energy σ_s as computed from Volmer's equation. Units of σ_s are erg cm^{-2}.

Temperature ($^\circ C$)	0	-10	-20	-30	-40	-50
Krastanow's σ_s	10.0	10.2	10.4	10.6	10.8	11.0
Corrected σ_s	10.0	9.6	9.1	8.5	7.7	6.8

Whereas Krastanow's values increase slowly with decreasing temperature, the temperature-corrected values decrease appreciably. That the latter sort of temperature dependence is the more reasonable would seem to follow from Dorsch and Boyd's (1951) x-ray diffraction studies, which indicate that as the degree of supercooling of water increases, the liquid becomes increasingly ice-like in structure. And as the structures of the two phases grow increasingly more similar, it should follow that the surface free energy of the interface between the two phases should decrease towards the zero value it must exhibit in the limit of complete isomorphism. Consequently the present revision of Krastanow's computation must be regarded as more nearly correct than the original values and will be used later in Section 10. Note that in the neighborhood of the -40C point, Krastanow's value is about 40 per cent too large, if the present revision is taken as the reference value.

Although Krastanow's estimates of σ_S were substantially in error, it must next be noted that since σ_S and L_f enter the Gibbs-Thomson equation only in the form of the ratio σ_S/L_f, and since exactly this ratio forms the left side of (9), Krastanow's errors in σ_S and L_f inevitably cancel each other exactly as far as any calculations of r_c from (5) is concerned. Nevertheless, F_c varies as $\sigma_S r_c^2$, so Krastanow's roughly 40 per cent overestimate of σ_S itself near -40C would still remain to throw off any nucleation rate calculations based on his results. It can be seen that some extenuating remarks might be made along the same line about Lafargue's (1951) calculation; but Lafargue mixed a 0C value of L_f with a value of σ_S which appears to have been interpolated linearly between Krastanow's 0C value and his -40C value. This somewhat undoes the work of one error canceling the other, so the point will not be amplified here, especially since Lafargue's whole approach is fundamentally unsound.

Having examined in some detail, and refined in one way, the Volmer-Krastanow method for estimating σ_s, attention will next be turned to a second method, first used in a meteorological application by Mason (1952). Mason's approach was as follows: He computed, using crystallographic data for ice, the total number of hydrogen bonds per unit area of a (0001) plane in ice, combined this with an estimate of the energy required to break one hydrogen bond, and therefrom determined the cleavage work per unit area required to pull an ice crystal apart perpendicular to the basal plane. Since this cleavage process creates two units of new surface area per unit area of basal plane, he identified one-half of the computed cleavage work (one-half of 204 erg cm^{-2} or 102 erg cm^{-2}) with σ_s', the specific surface free energy of ice against water vapor. Next he implicitly introduced Antonov's rule to obtain σ_s by subtracting the specific surface free energy of water against vapor from the 102 erg cm^{-2}. Using a value of 80 erg cm^{-2} for the surface tension of water at -40C, he obtained 22 erg cm^{-2} for σ_s. This value, then, underlies the results shown in Table 1 above. In view of the extreme sensitivity of calculated J values to the value used for σ_s, it is immediately disturbing to see that Mason's estimate is about three times as large as that which has been obtained above for -40C from a refinement of the Volmer-Krastanow method. This discrepancy demands that a careful evaluation of Mason's method of estimating σ_s be carried out, for although it has been emphasized above that the Volmer-Krastanow method remains open to serious question, choice between it and Mason's method cannot be made until the latter's validity is also assessed.

A first, and rather obvious question concerns the value which Mason took for σ_ℓ at -40C, namely 80 erg cm^{-2}. Perhaps, although he did not so state, Mason may have been influenced in this choice by a suggestion due to Sander and Damköhler (1943) to the effect that a value of about 78 erg cm^{-2} is required for σ_l near -40C to make certain experimental data on water vapor nucleation agree with theory. Bradley (1951) as well as LaMer and Pound (1951) have suggested that the decrease in σ_l below values extrapolated from experimental data above 0C may actually have been due to the effect of high surface curvature of the water nuclei involved. This explanation seems quite plausible to the writer (see comments at the end of this Section on a similar phenomenon in ice nuclei). If true, then it is definitely incorrect to make size correction in σ_l and then use this in Antonov's rule as has to be done in Mason's approach. Fortunately, some observational data exist to throw light on this question. Hacker (1951) has recently carried out an excellent experimental study of σ_l for water supercooled down to as low as -22C. His results are in very good agreement with the International Critical Tables to as far as the latter's data extend, -10C, and confirm the existence of the slight inflection point in $\sigma_l(T)$ near 0C that can be discerned in the I.C.T. values. Hacker's results definitely contradict the deductions of Sander and Damköhler (to the extent that the latter investigators' conclusions are applied to plane surfaces of water rather than to highly curved surfaces), for near -20C, Hacker's curve is curving slightly upward while Sander and Damköhler's is curving downward and lies already well below Hacker's absolute values. It may be mentioned that there is little ground for questioning Hacker's results on the basis that surface contamination might have affected his results, since contamination can easily lower surface tensions, but almost never raises them.

An extrapolation of Hacker's experimental curve to -40C, preserving the slight curvature of the 0C to -22C range, yields a value of about 84 erg cm^{-2}; so it appears necessary to alter Mason's value of 80 erg cm^{-2}, and hence in turn to revise immediately his value of σ_s from 102 - 80 = 22 erg cm^{-2} to

$102 - 84 = 18$ erg cm^{-2}. This rather slight revision in σ_S, it must be noted, has marked effects on calculated values of J and raises the theoretically predicted transition temperature by about 6 Centigrade degrees. It is clear that rather slight changes in one's basis for assigning numerical values to either σ_s' or σ_ℓ will have rather large effects on σ_S since the latter is, unfortunately, obtained from Antonov's rule as a small difference, $\sigma_s' - \sigma_\ell$, in two large terms.

The above revision has sent the present estimate of σ_S downward to improve somewhat the agreement between the Volmer-Krastanow estimate and that obtained from the cleavage-work approach. The sensitivity of σ_S to the calculated value of σ_S' requires that the latter quantity be scrutinized next. There appears to be no possibility of revising Mason's purely crystallographic arguments concerning the density of hydrogen bonds per unit area of a (0001) plane, a density which can be expressed inversely as an area per bond of 1.77×10^{-15} cm^2; but two objections must be raised against his method of calculating the the energy per bond.

Mason follows Pauling (1940, p. 304) in assigning a value of 4500 cal mole^{-1} to the hydrogen bond energy at 0C, but then states with no explanation that the corresponding value at -40C should be about 5100 cal mole^{-1}. Now the temperature variation of the heat of sublimation (quantity from which the hydrogen bond energy is determined by Pauling's argument) can be estimated from Kirchoff's equation applied now to the solid-vapor transition,

$$\left(\frac{\partial L_s}{\partial T}\right)_p = c_{pv} - c_{ps}$$

where c_{pv} and c_{ps} are the specific heats at constant pressure for the vapor and solid phases respectively. Near 0C, $c_{pv} = 0.443$ cal gm^{-1}deg^{-1} and $c_{ps} = 0.468$ cal gm^{-1}deg^{-1}, so $(\partial L_s/\partial T)_p \simeq -0.025$ cal gm^{-1}deg^{-1}. Both c_{pv} and c_{ps} decrease with T, but in such a way that their difference remains nearly constant. Hence, extrapolating to -40C from the 0C value, $L_s = 677$ cal gm^{-1}, one finds that near -40C $L_s \approx 678$ cal gm^{-1}. This change represents an increase of less than 0.2 per cent over the 0C value, in serious disagreement with Mason's roughly 13 per cent boost in the hydrogen bond energy over this temperature interval.

Since the discrepancy between the above thermodynamic estimate of temperature effect on L_s and Mason's unexplained adjustment is so large and has a marked effect on the calculated value of σ_s, it is fortunate that at least a crude independent check can be effected as follows: The coefficient of expansion of ice is about 5×10^{-5} deg^{-1}, so the 40 degree temperature change from 0C to -40C will decrease all lattice distances by about two parts per thousand if the effects of the slight anisotropy of ice are ignored. Now by Badger's rule (Pauling, 1940, p. 171), the force constant k_0 for a bond varies about as d^{-3}, where d is the pertinent interatomic distance. Since the range of forces here involved is only of the order of d itself, the work of breaking a bond is of the order of k_0d^2, or $d^{-3}d^2$, or d^{-1}. Badger's rule is only an empirical relationship, but that it yields tolerably good approximations can be shown by checking it against heats of dissociation of two different hydrogen-bonded substances having known bond distances (e.g., water and formic acid dimer). Combining the thermal expansion datum with Badger's rule, one predicts that the bond energy in ice should increase by about 0.2 per cent, just the value estimated on purely thermodynamic grounds above.

Since Mason gave no justification for his 13 per cent increase in the bond energy associated with the temperature change from 0C to -40C, and since two independent estimates assign it a value of only about 0.2 per cent, it appears necessary to reject Mason's figure of 5100 cal mole^{-1} in favor of the 0C value of 4500 cal mole^{-1} for the hydrogen bond energy per mole (simply ignoring the here predicted 0.2 per cent increase at -40C). This revision of Mason's estimate of σ_s' yields a value of $102(4500/5100) \approx 90$ erg cm^{-2}. Applying Antonov's rule and using $\sigma_\ell = 84$ erg cm^{-2} at -40C, one now gets only 6 erg cm^{-2} for a second-revised value of σ_S. This revision has sent σ_S below the revised Volmer-Krastanow value of 7.7 erg cm^{-2}.

However, a further error appears to have entered Mason's calculation of σ_S', and this error more than cancels the two errors now cited in his calculation. In computing the work that must be expended in cleaving an ice crystal parallel to the basal plane, Mason took account of only a part of the total bond energy, that ascribable to hydrogen bonding. That is, the value of 4500 cal mole^{-1} which he quotes from Pauling was obtained in turn by Pauling from the 12,200 cal mole^{-1} heat of sublimation of ice by observing that only about three-fourths of the total bond energy in an ice crystal is due to hydrogen bonding. The remaining one-fourth is due to van der Waals forces. Now in the conceptual experiment of cleaving an ice crystal, work would be done both in breaking hydrogen bonds and in separating neighboring molecules against the van der Waals attractions, so Mason was incorrect in ignoring the latter. The van der Waals attractions here in question are mainly of the type known as London disperson forces and arise in ice because of dipole-dipole interactions between adjacent oxygens. Fluctuations in the instantaneous dipole moment of one oxygen nucleus and its surrounding electron cloud induce instantaneous dipoles in neighboring oxygens and the time average of these fluctuating dipole-induced-dipole interactions constitutes an attractive effect. The exact nature of these forces is quite pertinent here because all of the available electrons in water may be regarded as surrounding the oxygen nuclei so that it becomes clear that the effective areal density of van der Waals bonds on a (0001) plane will be identical with that of the hydrogen bonds (since we may ignore all but nearest-neighbor interactions). The two types of bonding will, in fact, act coaxially along the oxygen-oxygen axes. Hence Mason's figure of 4500 cal mole^{-1} has only to be replaced by 6100 cal mole^{-1} to give a new estimate for σ_S' of 90(6100/4500)=122 erg cm^{-2}.

Applying Antonov's rule as before, one gets $\sigma_s = 38$ erg cm^{-2} as a final revised value resulting from Mason's approach.

Neglect of the van der Waals bonding was the most numerically serious error in Mason's work and is seen to lead to a value of σ_s which is about five times greater than the revised Volmer-Krastanow value for the same temperature. This large discrepancy in values of σ_s predicted by the two available methods leads to vastly different values of J near -40C, as will be shown below, and demands that search be made for still further refinements in the two calculational approaches so that the discrepancy may be reduced. It would, in particular, be very helpful even to know if the revised Volmer-Krastanow method somehow tends to underestimate σ_s or if the revised Mason method tends to overestimate the same quantity. A comment will next be made concerning the latter possibility.

In estimating the cleavage work in the way that gave Mason a value of 102 erg cm^{-2} for σ_s' and which has here yielded 122 erg cm^{-2}, no explicit allowance has been made for the reduction in the work of separation occasioned by the distortion of the lattice in the vicinity of the two newly created (0001) faces. The local density of atoms in the surface layer of a crystal is slightly lower than the value characteristic of the deep interior, and as a result a newly created surface of the sort envisioned in the cleavage operation will relax into a state of lower potential energy during the separation following cleavage. The result is (Brown, 1947; Shuttleworth, 1949) that the net cleavage work is reduced by an amount dependent upon the degree of surface distortion peculiar to the crystalline substance in question. Shuttleworth has succeeded in calculating this reduction term for the case of inert-gas crystals near absolute zero, and finds that it is of the order of only a few per cent of the gross cleavage work. However, Shuttleworth observes that for a crystal in which permanent dipoles contribute to the total bonding, this reduction term will become appreciably larger, though by an amount which he indicates is not easily computed. Since the ice lattice is chiefly held together by hydrogen bonds of the permanent dipole type, it would seem to follow that one must obtain a too-large value of σ_s' if no reduction is applied to the cleavage work to allow for surface distortion. This would mean that 38 erg cm^{-2} would, in turn, be an overestimate of σ_s .

Although the writer has not succeeded in making any precise determination of the distortion correction, the following crude argument is offered as an indication of the order of magnitude of the effect: One can make a theoretical calculation of σ_ℓ by the cleavage-work method used above; but to get σ_ℓ one must, of course base the calculation on L_v rather than L_s. The result for OC is 107 erg cm^{-2}, which is 32 erg cm^{-2} greater than the known value of 75 erg cm^{-2}. At -40C one gets 112 erg cm^{-2}, which exceeds by 28 erg cm^{-2} the -40C value used here on the basis of Hacker's study. Since the sort of surface distortion which occurs in a crystal lattice also occurs in a liquid (see, for example, Brown, 1947), one may take 30 erg cm^{-2} as an average distortion energy for liquid water over the temperature range of interest here. That this is a percentually very much larger correction than the distortion correction Shuttleworth found for inert-gas crystals is not surprising in view of the very different force laws involved in the bonding of the two types of substances; but whether this figure may be regarded as a close estimate of the distortion correction cannot be said to be certain. It will be a good estimate only if the cleavage calculation upon which the uncorrected values of σ_ℓ were based do take appropriate account of all other factors. The writer proceeds on the assumption that the latter is so.

Since the dipole and higher multipole binding in water substance involves significant interactions out to and possibly beyond next-nearest neighbors (Campbell, 1952), one must expect that the surface structure in water would be somewhat more open than that of ice since in water only short-range order exists, while in ice long-range order prevails. Consequently the distortion energy in ice must be slightly less than that in water, and roughly in inverse proportion to the latent heats of vaporization of the two phases. Hence, the distortion correction in ice may be taken here as about $30(L_v/L_s)$ ≈ 26 erg cm^{-2} for the temperature range from 0C to -40C. Applying this correction to the previously obtained value $\sigma_s' = 122$ erg cm^{-2} one gets 96 erg cm^{-2} as a crudely distortion-corrected estimate of the specific free energy of a vapor-ice interface.

Two distinct values have now been found for σ_s' from the cleavage-work approach, 122 erg cm^{-2} as a value uncorrected for distortion, and 96 erg cm^{-2} as a value very roughly corrected for distortion. Using Antonov's rule with values of σ_ℓ taken from Hacker (1951) and from a smooth extrapolation to -50C of Hacker's data, one gets the two sets of σ_s values shown in Table 3. For reference, the first line contains the σ_ℓ values used in the calculations.

Table 3. Values of σ_s in erg cm^{-2} calculated from the work of cleaving an ice crystal along a (0001) plane.

Temperature (°C)	0	-10	-20	-30	-40	-50
Value of σ_ℓ used (erg cm^{-2})	75	77	80	82	84	86
σ_s uncorrected for distortion energy	49	45	43	40	38	36
σ_s "corrected" for distortion energy	21	19	16	14	12	10

A last point to be considered under the heading of surface free energy of a water-ice interface concerns the question of the size-dependence of σ_s. It has been argued theoretically (e.g., Tolman, 1948) that surface energy must in general be a function of surface curvature. Indeed, the sort of simple molecular model in terms of which the r-dependence of L_f was obtained earlier here demands r-dependence also in σ_s since both of these parameters are largely determined by surface binding forces and the net effect of the latter is dependent upon surface curvature. LaMer and Pound (1951) have considered the experimental evidence for a decrease of surface tension of liquid water with decreasing radius of surface curvature and have discerned what may be such an effect in the experimental data of Sander and Damköhler (1943). Bradley (1940) made a calculation based on an inverse-seventh power law of attraction inserted into the Laplacian theory of capillarity and concluded that the surface free energy might drop by slightly less than 10 per cent at radii equal to ten molecular diameters, and by perhaps 13 per cent for drops with radii equal to only five molecular diameters (order of magnitude of critical ice embryos). More recently, Benson and Shuttleworth (1951) have made a similar calculation except that they included repulsive interactions. They found that for clusters of as few as thirteen molecules the size-reduction amounts to perhaps 15 per cent of the plane-surface value.

The fairly close numerical agreement between Bradley's and Benson and Shuttleworth's estimates of 10-15 per cent for the particle size range here involved, coupled with the further agreement between this estimate and the writer's size correction for the parameter L_f (Section 5 above) has led him to treat σ_S/L_f as size-independent in the Gibbs-Thomson equation (6). This leaves just the explicit factor of σ_S in (4) to produce net size dependence in the nucleation rates, and the writer chooses to employ a uniform 10 per cent reduction in σ_S whenever F_c is being computed, since the embryo radii are in just the size range where the above evidence suggests a correction of this order magnitude. Clearly there is room for improvement here, but it does not seem likely that much will be possible until a more complete theoretical treatment of surface energy of small aggregates is forthcoming.

8. The nuclear shape factor g

Once all parameters entering the Gibbs-Thomson equation are specified, the value of F_c is still dependent upon the shape factor g in (4). Mason chose $g \gtrsim 23$, the value appropriate to an hexagonal prism whose height equals three times its apical semidiameter, but he did not discuss the basis for this particular choice. Since all of the thermodynamic arguments that underlie the Gibbs-Thomson equation assume spherical nuclei, and since g for a sphere is only $4\pi \approx 12.6$, the use of any other value calls for some justification. As soon, however, as one gives explicit attention to this matter he recognizes that here is still another of the numerous details of nucleation theory which pose fairly subtle problems. In considering nuclear shapes, one must cope with the constraint imposed by the lattice geometry characteristic of ice; and for such small crystallites as those comprising nuclei in supercooled water near -40C it is not clear that one can choose arbitrarily either a sphere or any other shape. One guiding principle here is that the most probable nuclear shape should be that which is both representable by a microlattice and is consistent with the requirement that the total free energy shall be a minimum for the given number of member molecules. By analogy with gross crystal morphology one would expect that the crystal faces of high specific surface free energy would rapidly grow out, leaving best developed the faces of low specific free energy. Since Weickmann (1947) has clearly established the dominance of elongated hexagonal prisms near the -40C point, one concludes that near that temperature the basal planes must be charactized by somewhat larger specific surface free energy than are the prism faces. It follows (really by direct deduction from Weickmann's observations) that the preferred shape for nuclei near -40C ought to be elongated prisms, unless curvature effects somehow alter this problem seriously. Since Mason's choice of g corresponds to a shape that might be built up from the basic lattice geometry of ice while a sphere does not (in the limit of aggregates of nuclear size), and because furthermore the same g seems consistent with Weickmann's observations on macroscopic crystals, the writer chooses to follow Mason in using $g \approx 23$.

As for the implications of inconsistency this choice seems to introduce in view of the spherical shapes assumed in all underlying thermodynamic arguments, the writer would make the following observation: It has been pointed out earlier that (4) is correct only as long as edge energies are unimportant; and the ratio of the contribution of edge energies to that of surface energies grows large for exactly the size limit near which one works in nucleation theory. It is of double interest, then, to note that in Benson and Shuttleworth's (1951) analysis of the surface energy of small nuclei, their term which represents the contribution of edge energy to the total surface energy of a polyhedral cluster can be shown to comprise a term of identical functional form and approximately equal numerical magnitude as that which has been discussed above at the end of Section 7 in connection with the size-dependence of σ_s. That is, if one uses a value of σ_s corrected for size-dependence, it appears that he is essentially making an edge-energy correction for what is in microscopic reality a polyhedral crystallite rather than a true sphere.

9. Activation energy for self-diffusion

The most essential difference between the solid phase and the liquid phase of a given substance is that in the former, long-range order exists in the form of a truly crystalline structure, while in the latter only a short-range order exists. Yet in many liquids, of which water is an excellent example, this short-range order is well enough developed that one seems forced to regard each molecule as being rather well locked into a local structure which in the case of water is known to be tetrahedrally bonded. In view of this tendency towards a crystal-like local structure, molecules cannot move in a truly gas-like fashion among each other in a liquid. Hence the phenomena of self-diffusion and viscosity come to depend upon the probability with which an individual molecule may break one or more of the bonds which hold it to its nearest neighbors preparatory to moving relative to the local structure. The energy A required to thus attain the more mobile state of higher potential energy is drawn from the thermal energy distribution by the mechanism of random vibrational collisions, and the fractional probability that a given liquid molecule may have acquired this so-called "activation energy for self-diffusion" is given by the factor exp(-A/kT). This probability factor enters into the nucleation equation because each molecule (including the last one needed to just attain critical size) must first free itself from the liquid structure near the water-ice interface and then diffuse from the liquid region over onto the crystal lattice. The activation energy barrier may be thought of loosely as being made up of the work of breaking one intermolecular bond prior to the molecule's chance rotation into an orientation compatible with entry into the local lattice plus the work done during the very small linear translation then needed to lift the molecule from the bottom of a potential well close to its former liquid neighbors up to the plateau between that well and the potential well close to its future crystalline neighbors. In the limit of very low temperatures, where F_c becomes negligibly small, the rate of growth of embryos becomes limited almost entirely by the diffusional barrier, and a true ice lattice may have to give way to a vitreous form of the solid phase.

Since exactly the same activation energy enters, in an inverse manner, into viscous processes it becomes possible to determine A from empirical viscosity data. Although there have been proposed many different expressions for describing the temperature dependence of viscosity (Partington, 1951), the most widely accepted on both theoretical and observational grounds is

$$\eta = Ce^{(A/kT)} \tag{11}$$

where η is the coefficient of viscosity and C is a constant. Mason (1952) made use of (11) to determine A using viscosity data of White and Twining (1913). He obtained the value $A=3.3\times10^{-13}$ ergs, and it is of immediate interest to note that this is of the order of magnitude of the energy per bond in water, as would be expected on the basis of the physical picture suggested above.

It should be mentioned here that Krastanow (1941) gave an estimate for A of $2x10^{10}$ erg gm^{-1} or about $6x10^{-13}$ ergs per molecule, which he obtained from a suggestion due to Volmer (1939) that A must be somewhat less than the molecular heat of vaporization of the substance in question. That Krastanow's value is about twice as large as that found by Mason from (11) is due to the fact that an estimate based upon L_v (Krastanow actually used 500 cal gm^{-1}) inevitably measures the energy needed to break two intermolecular bonds, whereas diffusion actually appears to proceed primarily by a sequence of single-bond ruptures followed by rotations about the remaining bond, even in ice (Owston, 1951).

To complete this brief examination of previous treatments of A in nucleation studies, it may be recalled that one of the objections raised in Section 3 to the calculations of Fisher, Hollomon, and Turnbull (1949) concerned their complete omission of a term of the form exp(-A/kT) in their nucleation equation. In terms of the physical picture suggested above it seems clear that this omission left out an effect which, especially for large degrees of supercooling, assumes appreciable importance in inhibiting embryo growth. Finally, it may be noted in passing that a diffusional barrier does not affect nucleation of either liquid or solid embryos forming in supersaturated vapor because the nearest-neighbor distance in a vapor is generally so great as to preclude the sort of interactions which inhibit diffusion in a liquid.

In estimating A, Mason's approach is followed here. However, Mason did not take cognizance of the fact that A increases with decreasing temperature due to the increasing degree of order in the liquid structure at lower temperatures. From viscosity data given by Dorsey (1940, Tables 82, 85), the writer has computed A(T) in the temperature range from -10C to 70C. The results are shown in Figure 2 as the solid portion of the curve. Mason's value of $3.3x10^{-13}$ erg is seen to correspond to a temperature of about 5C, while in the temperature range of interest in the problem, A is clearly going to be

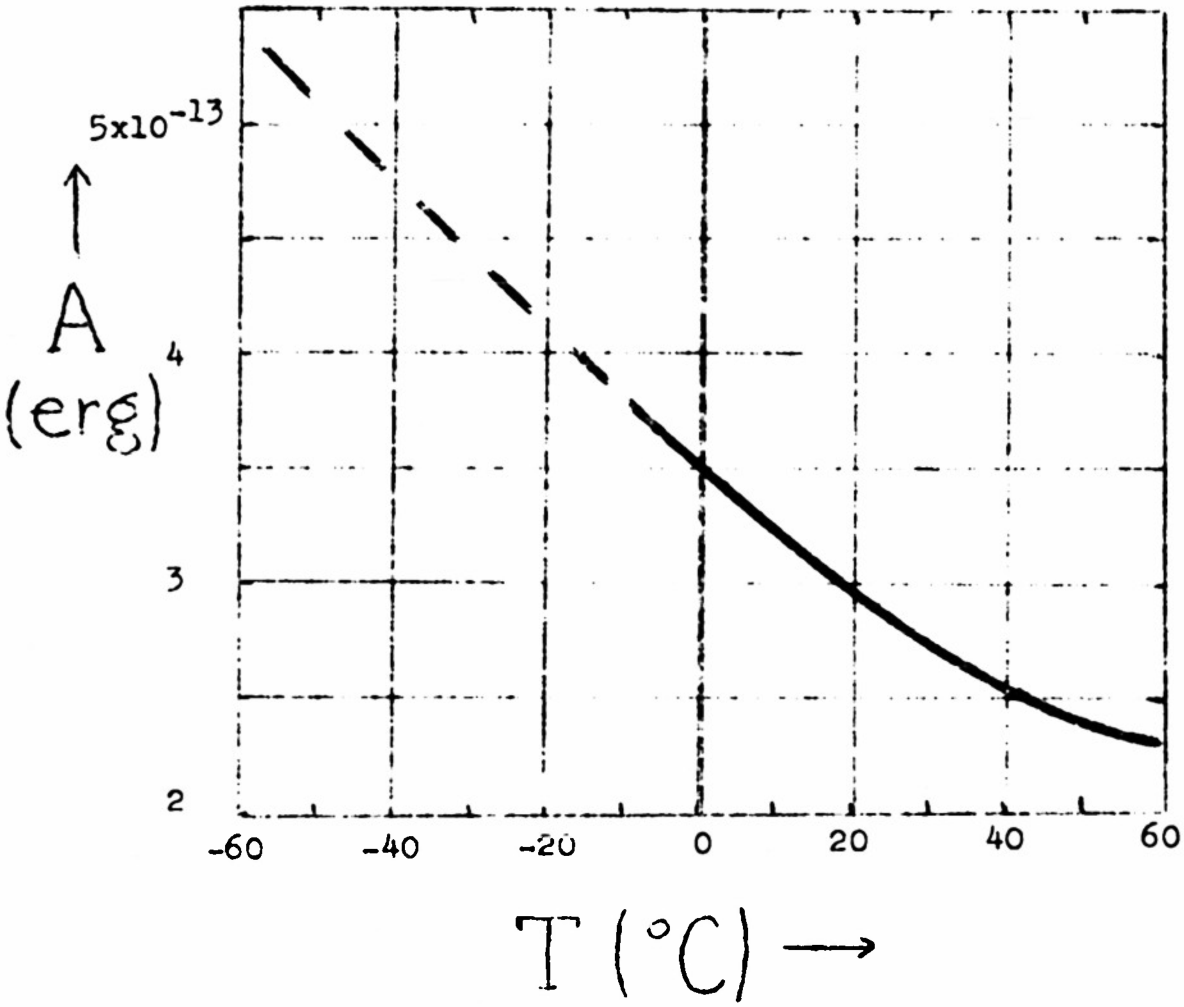

Figure 2. Temperature dependence of the activation energy for self-diffusion in water. A is given in units of ergs per molecule. Values from 60C down to -10C calculated from empirical viscosity data (Dorsey). Values from -10C down to -50C obtained by linear extrapolation.

larger. In view of the fact that the functional form of (11) is not indisputably established, the writer has only felt justified in making a simple linear extrapolation down to the temperature limits of interest here. This procedure probably tends to underestimate slightly the activation energy barrier, but is clearly an improvement over the use of a constant value corresponding to a temperature near 0C.

10. Calculations

The primary objective of the present study has been to determine, if possible, whether the -40C transition can be explained theoretically in terms of the homogeneous nucleation process. The test of this hypothesis consists in calculating values of J from (3), (4), and (6) for water drops of specified size and for a number of different temperatures to see what degree of supercooling is required to raise the nucleation rate per drop per second to the order of unity (cf. discussion of Table 1 in Section 3 above). This will now be done, using the revised numerical values of the several parameters discussed in Sections 5 through 9 above.

In the calculations, the value of n in (3) will be taken to be the number of water molecules in an isolated drop of 10 micron radius. From the values of J here calculated, one may readily obtain the corresponding values for smaller or larger radii to form a table of the form of Table 1, since J varies linearly with n. A radius of 10 microns is selected here as being typical of the drop size reported in laboratory studies of the -40C transition (e.g., Schaefer, 1949). It also serves reasonably well to represent the natural cloud physical situation.

Since (3) is transcendental in T, one cannot simply put $\log_{10}J = 0$ and solve directly for T to determine the theoretical transition temperature. Instead, one may compute and plot $\log_{10}J(T)$ and then read off the value of T where the curve crosses the axis of abscissas. This has been done here in

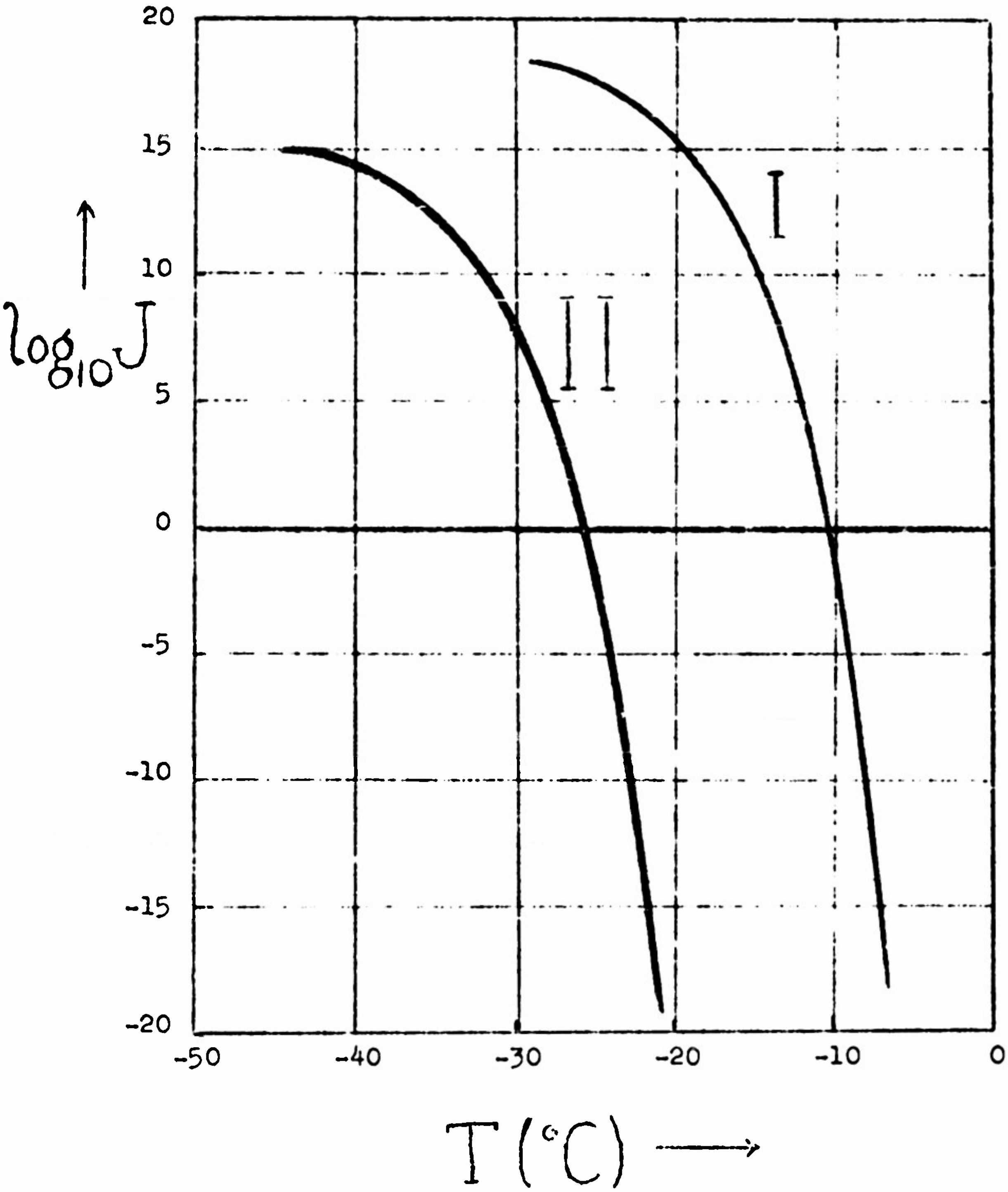

Figure 3. Temperature dependence of the nucleation rate J for supercooled water drops of 10 micron radius. Curve I was computed using σ_s as estimated by the revised Volmer-Krastanow method; Curve II was computed using σ_s as estimated by the revised Mason method with an approximate correction for surface distortion energy.

three separate series of calculations, one corresponding to each one of the methods of estimating σ_S . The results, displayed in part in Figure 3, are as follows:

(1) Using σ_S as obtained by the revised Volmer-Krastanow method (Table 2), one gets curve I of Figure 3. It is seen that the temperature for spontaneous nucleation of 10 micron drops is predicted to be about -10C according to this calculation.

(2) Next, using values of σ_S obtained from the present revision of Mason's approach (Table 3) one obtains values of J which are so minute as to preclude spontaneous nucleation anywhere near -40C. The lowest temperature to which the writer extended this part of the calculations was -70C, and even for that extreme degree of supercooling, a drop of 10 micron radius would experience a nucleation only once in about 10^{68} seconds, if this second set of σ_S values were correct. The age of the universe is believed to be of the order of 10^{17} seconds. Such low nucleation rates cannot conveniently be shown in Figure 3, and would clearly be of no meteorological interest anyway.

(3) Finally, using the values of σ_S based on the present revision of Mason's approach but corrected very roughly for distortion effects in the manner indicated earlier (Table 3), one gets the curve shown as II in Figure 3, from which the theoretically predicted transition temperature is found to be about -26C.

Before discussing these results, one additional calculation will be examined. Fisher, Hollomon, and Turnbull (1949) have used (3) to compute the value which σ_S must have if the -40C transition really is due to homogeneous nucleation. In Section 3 above, several objections to their calculation have been noted. It is of interest here to repeat that calculation on the basis of such revisions as have been made in the course of the present study (excepting, of course, revisions in methods of calculating σ_S itself). Assuming that the laboratory observations of the -40C transition apply to drops of 10 micron radius, one finds by this sort of inverse calculation that a value of σ_s of 18 erg cm^{-2} would bring the present theory into accord with laboratory observations. This figure is to be compared with the -40C values of 7.7, 38, and 12 erg cm^{-2} obtained in this study by three different methods, and with the value of 33 erg cm^{-2} deduced by Fisher, Hollomon, and Turnbull.

11. Discussion.

On the basis of a rather large number of revisions of previous efforts to examine the -40C problem, three separate calculations have been made here employing three different sets of estimated values of σ_s, the variable having dominant numerical influence on the theoretical nucleation rates.

The first of these calculations (Curve I, Figure 3) implies a far too efficient nucleation process. If all of the other parameters controlling J can be trusted (and they can certainly be trusted to far greater extent than can σ_s), then one can conclude that the values of σ_s estimated by the Volmer-Krastanow method must surely be lower than the correct values because it is well known that liquid water drops often exist in clouds at temperatures substantially below -10C. It must be recalled that no really firm basis for accepting the Volmer-Krastanow method for estimating σ_s has yet been given, although the writer has suggested earlier here one way in which it can at least be rendered qualitatively plausible.

The second calculation predicts an effectively zero nucleation rate down to degrees of supercooling well beyond any of meteorological interest. That is, when the writer calculates σ_s after the manner suggested by Mason, but with Mason's apparent errors corrected in the best way recognized by the writer, the implied nucleation rates are found to fail completely to account for a -40C transition. This plus the results of the first calculation seems to place the burden of the argument squarely on the correction for distortion energy in the cleavage computations.

In the third calculation, where a crude, though at least not arbitrary correction for the lattice distortion effect has been included, the predicted transition temperature still falls outside the range of observed transition points, though by an amount which is only about half as great as the discrepancy for the first of the three calculations. The phenomenal increase in computed nucleation efficiency that accompanies the application of the distortion energy correction is very disquieting in view of the uncertain grounds on which a distortion correction was made here. Consequently it becomes important to examine the possibility that one could make some more straightforward attack on the problem of determining the distortion energy.

If one had experimental data concerning the lattice expansion in the outer two or three molecular layers near an ice surface, he might calculate the distortion energy fairly accurately from the known compressibility coefficient of ice; but unfortunately x-ray data inevitably provide only a picture of the average structure down to many tens of molecular or atomic distances. Perhaps electron diffraction methods hold somewhat more promise, but the difficulty in adequately preparing a sample surface in the case of ice would probably be a limiting factor here.

On the theoretical side, it might be hoped that a direct calculation modeled upon that made by Shuttleworth for inert-gas crystals would be the answer, and this is indeed so in principle. In fact, however, such a calculation would be extremely difficult. Following Shuttleworth, one would seek a gener-

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On the theoretical side, it might be hoped that a direct calculation modeled upon that made by Shuttleworth for inert-gas crystals would be the answer, and this is indeed so in principle. In fact, however, such a calculation would be extremely difficult. Following Shuttleworth, one would seek a general expression for the potential energy of a surface molecular plane with respect to all of the rest of the crystal, minimize this with respect to the interplane distance, solve for the implied equilibrium interplane distance, and then insert this back into the general energy expression to compute the reduction in energy due to surface distortion. But whereas the interatomic attractive potential in an inert-gas crystal falls off as r^{-6}, that for dipolar ice would contain terms falling off only as r^{-3}, so one would have to minimize jointly the potential energy of at least the two uppermost planes of water molecules, and this might be only a first approximation. This complication would not be so serious by itself, but each of these potentials involved would have to be expressed as a sum over the lattice of a Taylor series expansion (multipole expansion) of the charge distribution around each H_2O molecule. Campbell (1952) has examined the problem of calculating the lattice energy of ice (for fixed intermolecular distances) in terms of multipoles, and has found that even when one includes up to fifth-order terms (e.g., octupole-octupole interactions) for nearest-neighbors the agreement with the corresponding thermodynamic data is unsatisfactory. Furthermore, Campbell found that interactions between next-nearest neighbors are still significant out to beyond third-order terms. From Campbell's Table II, one can see that this means that the potential energy for each molecule in a plane near the surface must contain some fifteen terms in the variable interplane distance; and since one must find a joint minimum for at least the first two interplane distances, it follows that at least thirty terms are involved in the function whose minimum would be sought. Finally a very serious further complication enters by virtue of the fact that these multipole interactions, unlike the dispersion forces (London, 1937) with which Shuttleworth dealt, are not simply additive, so the type of lattice sums which were usable in Shuttleworth's calculation are not applicable here.

In all, it seems questionable whether the heroic efforts that would have to be made to effect this lattice calculation of the distortion energy are meteorologically justifiable. This last step required to complete the theoretical exploration of the problem of homogeneous nucleation of supercooled water drops appears to be of an order of difficulty far exceeding that of any solid-state calculations that have yet been carried out for ice or other dipole crystals. Consequently the writer feels that the fact that even a crude estimate of the distortion has here yielded a theoretically predicted temperature of -26C may for the present be taken as a strong indication that the -40C transition is truly an effect of homogeneous nucleation, an effect whose precise nature cannot be specified quantitatively in the present state of knowledge of the solid-state physics of ice. Careful scrutiny of the present revisions of previous investigators' work will have to be made by others before this conclusion can be accepted; but if the present calculations can be regarded as essentially correct up to the last step of making the distortion correction, and if no experimental evidence clearly contradicting the homogeneous nucleation hypothesis is forthcoming, then there would seem to be strong enough grounds for concluding that -40C is the temperature to which water droplets of cloud-particle size must be supercooled in order that there shall be nearly unit probability of the formation of an ice embryo of critical size somewhere within each drop, that is, that the cloud there undergoes spontaneous nucleation.

13. A remark on the icing of aircraft

The theory of homogeneous nucleation may shed some light on one important aspect of the aircraft icing process. In those discussions of icing with which the writer happens to be familiar, no clear explanation seems to be offered for the reason why the accreted supercooled water freezes after deposition even though it may have remained liquid for a long period prior to entrance of the aircraft into the given cloud. Or, if an explanation is given, some allusion is made to the shock of the impact and the reader is reminded of the alleged role of mechanical disturbance in initiating freezing in bulk supercooled water.

If, as the writer has here been attempting to show, the existence of the supercooled cloud is primarily due to the negligibly small rate of homogeneous nucleation above -40C then the reason why water freezes after deposition though not before is that the free energy barrier to the formation of a critical embryo on which the crystallization may begin is no longer an obstacle to freezing when the drop impinges on the surface of the airfoil. If a sheet of ice is already present on the airfoil, the impinging supercooled water merely joins that ice lattice in the ordinary way in which water freezes on lattices of small curvature. If ice does not preexist, as at the moment of first penetration into the icing region, then the microscopic roughness of the airfoil surface, or perhaps some adsorbed foreign material, is almost certain to initiate freezing by heterogeneous nucleation *somewhere* within the water film covering the leading edge. Once a microscopic lattice is created *anywhere* along the wetted surface of the airfoil, freezing will spread epidemically throughout all portions of the water film continuous with the locus of nucleation. After that, the freezing of impinging drops occurs by the sort of process first outlined.

The essential difference between the film of water on the airfoil and the same mass of water in the form of many cloud drops is that in the former case only *one* successful nucleation event need occur within its total volume to produce complete crystallization, while in the latter case some supercooling will persist until there has occurred one nucleation event within *each* of the individual drops. That is, the difference is essentially topological, having to do with the connectedness of the water. If it is indeed true that average cloud drops cannot be expected to be nucleated once within their full lifetime of the order of minutes at temperatures much above -40C (recall general implications of Table 1), then one can understand why aircraft icing is observed above that temperature but is almost unknown below that temperature.

13. Summary

Previous investigations of the -40C transition in supercooled water drops have been shown to contain a variety of inaccuracies which have had marked effect on predicted nucleation rates. After a number of modifications were carried out in existing approaches to the homogeneous nucleation problem, three different estimates of the specific surface free energy of a water-ice interface were used to estimate the temperature dependence of the dropwise nucleation rate. Of the three results, the one in which the most confidence can be placed yielded a predicted transition temperature substantially too high, -26C, but was based on a correction for surface distortion effects that is recognized to be quite crude. There seems little immediate hope for gaining improved precision in the estimate of the distortion correction on theoretical grounds, since the required calculation poses very formidable difficulties.

The fact that one rough estimate of the distortion energy has led to a predicted transition threshold even as close to the observed value as -26C is tentatively taken to indicate that the -40C transition is an effect of homogeneous nucleation whose precise explanation will have to await further developments in the solid-state physics of ice.

14. Suggestion for future research

It would be of the greatest interest to have some sort of experimental determination of the surface free energy of a water-ice interface. Although a direct evaluation of this parameter for supercooled water seems quite out of question, it may not be entirely impossible to determine this quantity at the triple point of water by employing sufficiently elaborate thermostatic control. It should be clear from the previous discussions of the distortion energy correction that immeasurable improvement in one's understanding of the nucleation problem would result even from a reasonably accurate determination of σ_s at the triple point.

Acknowledgments

The writer wishes to thank his colleagues, Drs. R. E. Rundle and R. S. Hansen and Mr. M. Parasol, all of the Department of Chemistry, and Drs. G. C. Danielson and J. M. Keller of the Department of Physics of Iowa State College,

with each of whom the writer has held helpful discussions of certain aspects of the problems discussed in Part I.

II. On the Electrical Conductivity of the Lower Stratosphere

Abstract --The reality of the decrease of conductivity with height observed at the top of the *Explorer II* flight is supported by some apparently overlooked measurements made earlier by Idrac. The cause of this decrease is discussed and an hypothesis of convective updraft of Aitken nuclei from troposphere to stratosphere is examined. The hypothesis appears incapable of accounting for a steady-state worldwide population of stratospheric nuclei sufficient to satisfy existing observations. It is urged that Idrac's measurements be repeated on a more extensive basis using more modern sounding techniques.

1. Introduction

One of the many results of the 1935 stratosphere balloon flight of the *Explorer II* was the observation of a surprising decrease of atmospheric electrical conductivity with height through the top few kilometers (19-22 km) of that flight. Gish and Sherman (1936) have discussed this feature of the sounding and Gish (1939) has made some suggestions as to its possible origin; but no further attention seems to have been given this matter until Holzer and Saxon (1952) recently examined, on theoretical grounds, the current distribution that may be expected to exist above and around an active thunderstorm. They approached this problem in an effort to check the significance of the important thunderstorm electrical measurements made by Gish and Wait (1950).

Holzer and Saxon employed the assumption that atmospheric conductivity increases exponentially and hence monotonically with increasing height through the troposphere and stratosphere all of the way up to some conducting layer in the lower ionosphere. In making this assumption, these authors did not overlook the Gish and Sherman observations of a conductivity minimum, but they did choose to omit this feature from their analysis on the basis that it is not known whether this represents a commonly occurring condition of the lower stratosphere or whether it was an anomaly peculiar to the *Explorer II* sounding. Holzer and Saxon point out that a shallow layer of low conductivity would not alter their principal conclusions concerning the ionospheric destination of the currents measured by Gish and Wait (1950), but emphasize that such a layer could have a marked effect on certain other atmospheric electrical phenomena, notably the vertical field fluctuations observable at the earth's surface at distances of the order of many tens of kilometers from active thunderstorms.

2. Earlier evidence for a stratospheric conductivity decrease

Holzer and Saxon's discussion has pointed up the uncertainty as to whether a stratum of low conductivity is a common, or indeed even a real feature of the stratosphere and has prompted the present writer to call attention to an earlier and apparently forgotten study of the electrical state of the lower stratosphere in which there was found evidence for a decrease of conductivity similar to that found in the Explorer II sounding. Idrac (1926) made a number of balloon soundings of the vertical electric field intensity over Trappes, France during a single day in June, 1926. Three of his releases led to soundings extending above 13 km and in these three Idrac found that the field intensity, after decreasing in the characteristic manner through the troposphere, started increasing above the tropopause. The average field strength at 8 km for all of his flights for that day was only 2.3 v/m, while in the region above 13 km it reached values as high as 40 v/m. Assuming a uniform vertical current density for all heights reached by Idrac's balloons, one finds that these intensity values imply a conductivity decrease by a factor of almost twenty in going from 8 km up to this level of maximum local field strength above 13 km. Fortunately, one of Idrac's flights extended to 20 km and revealed that the field intensity decreased again above 16 km, falling to 1.2 v/m at 19 km, thus showing that the conductivity did not remain low that day throughout the vertical extent of the stratosphere over France.

These observations by Idrac seem not to have been known to Gish and Sherman, with the result that there has probably been less significance attached to the Explorer II results in the 19-22 km region than might otherwise have been the case. Idrac's findings seem particularly valuable in that they refer to a region remote from that in which the Explorer II flight was made and to a time several years earlier, thus casting doubt on any supposition that the sort of low conductivity stratum found by Gish and Sherman was an anomaly peculiar to that sounding. Furthermore, Idrac's measurements suggest that there may be only a rather thin layer of low conductivity in the stratosphere, while the Explorer II observations left this important point indeterminate. This latter contribution of Idrac's work strengthens the position taken by Holzer and Saxon (1952) with respect to the slight importance of any regions of low conductivity in altering the upward flow of positive current from thunderstorm to ionosphere, while the former contribution (indication of worldwide extent of the low conductivity layer) points to the need for further study of the suggestion made by Holzer and Saxon that such a layer may strongly influence surface field-strength fluctuations far from active thunderstorms and squall lines.

3. Possible causes of the conductivity minimum

Despite the lack of agreement between Idrac's and Gish and Sherman's observations of the altitude of the base of the region of low conductivity, their agreement as to the presence of such a region in the lower stratosphere would seem to justify some attempt to find an explanation for its existence. Atmospheric conductivity is almost entirely controlled by the small-ion density of the air, and this density is in turn controlled jointly by the rate of ion formation (by cosmic ray ionizations followed by molecular attachment) and by the rate of destruction (by recombination processes and by attachment to Aitken nuclei, forming relatively immobile large ions); hence one must search for some phenomenon capable of locally altering one or both of these rates in the stratum under consideration. There would appear to be no basis for believing that there might be any local decrease of cosmic ray bombardment here, nor any local anomaly in the molecular attachment rates or in the recombinative processes for small ions, so one is led to seek an explanation for the low conductivity in terms of the effect of some local concentration of nuclei in the lower stratosphere. Gish (1939), in first discussing this type of explanation, suggested the possible role of nitrogen pentoxide which has been detected spectroscopically in the region from 16 to 40 km. Gish (1951) has also noted that ozone was found to be unusually abundant near the top of the Explorer II sounding; but he has not indicated how either of these substances might ever appear in the form of particles large enough to serve as large-ion nuclei.

4. Convective transport of nuclei

The writer has been led to consider quite a different hypothesis which seems, at first inspection, qualitatively more probable than those advanced by Gish. This hypothesis would account for the presence of a stratum of Aitken nuclei in the lowest portion of the stratosphere in terms of injection of nucleus-rich air into the base of the stratosphere by thunderstorm updrafts that sweep the air up through the troposphere from the lower levels of higher nuclear density and then expel this air into the stable base of the isothermal region. The nuclei so added from time to time by thunderstorms around the world would not remain forever in the lower stratosphere but would slowly leave this region by virtue of the joint action of fall-out and turbulent diffusion. The critical test of the hypothesis thus becomes that of inquiring whether the processes of addition and removal might reasonably be expected to come to balance with a steady-state nuclei count at the base of the stratosphere sufficient to explain the sort of decreased electrical conductivity found by Idrac and by Gish and Sherman.

5. Thunderstorm heights

First it may be noted that the heights to which thunderstorms extend are in reasonable agreement with the convective hypothesis, at least for the Idrac observations of a low-conductivity layer with its base near 13 km. The average heights of the tops of thunderstorms observed by radar during the Thunderstorm Project (Byers and Braham, 1949) was slightly over 11 km, and 40 per cent of all observed storms built up to 13 km or above. It is, of course, no mere accident that the base of the stratosphere coincides closely with the maximum altitude reached by thunderstorm updrafts since the stable density distribution above the tropopause precludes appreciable growth into the stratosphere.

The location of the low-conductivity layer in the Explorer II sounding is higher than can be accounted for in terms of average thunderstorms of middle-latitudes, and particularly so for the November date on which the flight was made. Examination of the temperature distribution prevailing during the flight (Brombacher, 1936) reveals that a double tropopause existed over South Dakota on flight day. The lower inversion began at 11.5 km and the upper began at about 18.7 km. This plus the fact that the winds near the top of the flight were southwesterly suggests that the balloon may have been in air that had recently come from lower latitudes of the Pacific area where thunderstorm convection is better able to transport air to heights approaching those at which the Explorer II encountered the decrease of conductivity. However this necessity of an appeal to a tropical origin of the nuclei over South Dakota must be regarded as a weakness of the thunderstorm hypothesis and if further measurements of stratospheric conductivity should reveal that the average level of the minimum agrees more closely with that found by Gish and Sherman than with that indicated by Idrac's work, one could not even consider the convective explanation here proposed.

6. Rate of convective transport of nuclei

The first step in a quantitative check of the convective hypothesis consists in estimating the average worldwide rate of thunderstorm transport of nuclei up to the base of the stratosphere. Using data on the average vertical distribution of Aitken nuclei based on twenty-eight balloon flights in the troposphere (Landsberg, 1938), and combining these with some recent estimates of the vertical distribution of thunderstorm inflow rates (Braham, 1952), one finds that, during the entire lifetime of an average thunderstorm cell of the middle-latitude type considered by Braham, about 3×10^{20} nuclei may be expected to enter the updraft. Of this total, almost three-fourths of the nuclei are found to enter the cell in the 0-1 km layer. At greater heights, where the mass of air entrained is larger than in the surface layer, the nuclei count has fallen off so much that the weighted average influx of nuclei is much less than in the 0-1 km interval.

Not all of these 3×10^{20} nuclei are to be regarded as reaching the outflow region at the very top of the storm, however. A certain number will serve as condensation nuclei and will thus be largely removed by the precipitation process; but this number is so small compared to the total number of Aitken nuclei (most of which are too small to be activated for growth) that it may be ignored here. Second, relative motions of nuclei and cloud drops will remove some nuclei by accretion, but this mechanism will also be ignored here on the ground that the collection efficiency for this capture process will be very low in view of the small size of the nuclei. The third process, which cannot be ignored, is that of horizontal outflow of updraft air prior to its reaching the tropopause. Again Braham's data on mass-exchange in thunderstorms provides a basis for an estimate. Braham (1952) finds that of the total of 9.0×10^{10} kg of air entering an average storm throughout its duration, only 1.8 by 10^{10} kg flows out at the 200 mb level (about 12 km). Thus, one may regard only 1.8/9.0 of the total of 3×10^{20} nuclei, i.e., about 7×10^{19} nuclei, as being expelled from the storm top into the lower layers of the stratosphere. It must be admitted that present ignorance of the details of the kinematics of the outflow pattern at these levels leaves doubt as to whether even this latter number of nuclei may safely be assumed to remain at the outflow level rather than to subside back into the upper troposphere, but this assumption will be made here.

Taking the average lifetime of a thunderstorm cell as about one hour (Byers and Braham, 1949), and using Gish and Wait's (1950) estimate of 3×10^3 storms as the average instantaneous rate of occurrence of thunderstorms over the entire globe, one finds an average rate of stratospheric addition of 6×10^{19} nuclei per second for the whole world. Overlooking the fact that this rate of transport must certainly decrease rapidly with increasing latitude to nearly zero values in both polar regions, one finds that for the entire area of the earth, 5×10^{18} cm^2, the average rate of thunderstorm injection of nuclei into the base of the stratosphere may be of the order of 10 nuclei/cm^2 sec.

7. Rate of fall-out of nuclei

Having estimated the rate of addition of nuclei, the next step is to estimate the rate of removal in order to compare these two rates as a test of the convective hypothesis. Gish and Sherman (1936) have given estimates of the density of nuclei required to account for the low conductivity in the 19-22 km interval of their Explorer II measurements, so in spite of the fact that this interval lies several kilometers above the level to which one may expect thunderstorms to penetrate in middle latitudes, and in spite of the author's warning that not too much quantitative significance should be attached to their nuclei estimates, these values will be used here as the only available estimate of the nuclear densities in the lower stratosphere. Certain additional deductions can be made from Idrac's data, and note will be taken of these later.

Most Aitken nuclei are less than about 2×10^{-5} cm in diameter (Junge, 1951), so Stokes' law may be applied with reasonable accuracy. Assuming a mean density of 2 gm/cm^3 for the nuclear substances, the particles may be expected to have a maximum fall velocity of only about 10^{-3} cm/sec, i.e., less than a meter per day for even the largest. The average instantaneous rate of fall-out per unit horizontal area of the stratosphere is then given by the product of this velocity and the prevailing nuclear density, which we may take as 2×10^3 nuclei/cm^3 (Gish and Sherman, 1936). Thus the downward gravitational flux of nuclei is only about 2 nuclei/cm^{2}sec. This is almost an order of magnitude less than the estimated rate of addition of nuclei by updrafts, so if fall-out were the sole mechanism capable of removing the nuclei from the stratosphere, one could conclude that the convective hypothesis was confirmed by the above estimates; but in addition, downward turbulent diffusion must be considered.

8. Turbulent diffusion of nuclei

The rate of vertical turbulent diffusion of nuclei in a layer depends on the eddy diffusion coefficient D, and on the vertical density gradient of the nuclei, dn/dz. Lettau (1951, Fig. 2) gives 10^5 cm^2/sec for the diffusion coefficient at the 15 km level, and from Gish and Sherman (1936, Fig. 7) one finds the density gradient in the layer of low conductivity to be about 10^{-2} nuclei/cm^4. Hence for this combination of data the turbulent flux is

$$D \frac{dn}{dz} = (10^5 \mathrm{cm}^2 \mathrm{sec}^{-1})\,(10^{-2} \mathrm{cm}^{-4}) = 10^3 \mathrm{cm}^{-2} \mathrm{sec}^{-1}$$

downward. This rate is three orders of magnitude greater than the rate of fall-out, so it appears that one may quite safely neglect fall-out as compared with diffusion. But more pertinent to the present discussion is the fact that the estimated rate of downward diffusion of nuclei is some sixty times greater than the estimated rate of addition of nuclei by thunderstorms (15 nuclei/cm^2 sec.). One seems forced to conclude that the convective transport hypothesis is quantitatively inadequate for accounting for a uniform, worldwide stratum of high enough nuclear density to fit the Explorer II conductivity measurements.

9. Discussion

Having found this negative result in the effort to check the convective hypothesis, it is interesting to note that if one seeks points in the computations where some modification might be made, these appear to be almost entirely changes that only strengthen the evidence against the hypothesis.

First, the data on nuclear densities in the troposphere (Landsberg, 1923) were obtained from balloon flights made over well settled areas where industrial pollution tends to give counts unrepresentatively high for the world as a whole, so any revisions here would certainly lower the estimated convective transport rate.

Second, the assumption that all of the air diverging from the thunderstorms at the 200 mb level remained, along with its suspended nuclei, at the level of outflow cannot be defended too well. A thunderstorm that builds up to the tropopause probably succeeds in locally pushing up the stable overlying stratospheric air but complete intermixing of the outflow with stratospheric air, as assumed above, is a rather unlikely extreme. If any corrections could be made here they would undoubtedly lower the effective rate of convective addition of nuclei.

Third, an attempt to incorporate Idrac's findings into the estimate of the downward diffusion of nuclei from the underside of the stratum of low conductivity yields an even higher rate of removal than was found above from the data of Gish and Sherman. Idrac reports a nearly twenty-fold increase of field strength between 8 km and about 14 km, which implies a roughly equal factorial decrease of conductivity in this interval. Gish and Sherman (1936, Fig. 4), on the other hand, found a conductivity decrease of a factor of only two in the interval from 19 km to 22 km. This difference in implied nuclear gradients is thus seen to amount to about a factor of five, making it correspondingly more unlikely that thunderstorm updrafts are steadily counterbalancing downward diffusion of nuclei.

Fourth, one might choose to use the eddy diffusivity value corresponding to the interval in which the conductivity decreased in the Explorer II sounding (19-22 km) rather than to use the value for the 15 km level as was done above in an effort to simulate conditions prevailing just above the tropopause. Lettau (1951) gives $10^3 cm^2/sec$ for D at this level (down a hundredfold from D at 15 km), so combining this with the previously considered value of the density gradient one obtains an estimated diffusion rate of 10 nuclei/cm^2sec. This is just the estimated transport rate, so this fourth revision is the first one to favor the convective hypothesis. But since this revision requires that one deal with altitudes too great to match observed thunderstorm heights for any but tropical latitudes, it provides no real support for the convective hypothesis anyway. It is, however, interesting to note that Lettau (1951) has suggested that the very rapid decrease of D with height just above 15 km must tend to produce what he terms a "dust horizon" at this level, and cites some light-scattering observations in support of that contention. This theoretical and observational evidence for some sort of zone of accumulation just above the tropopause does give further support to the view that a layer of high nuclear density and hence low conductivity is the rule rather than the exception in the lower stratosphere but, does not clarify its ultimate origin.

In all, it would seem to have been shown here that the convective hypothesis for transport of nuclei to the stratosphere, though qualitatively quite plausible, is not quantitatively compatible with such observations of the conductivity minimum as exist at present.

10. Concluding remarks

That Idrac's observations of the vertical variation of the electric field intensity should constitute the only check on the decrease of conductivity with height in the lower stratosphere found in the Explorer II flight, and that even this check should have gone so long unnoticed seem regrettable.

Present-day balloon-sounding techniques should be readily capable of providing data on the behavior of the field up to almost 30 km. Hence the writer wishes to recommend that repetitions of Idrac's measurements be carried out at enough different localities and times to determine whether a layer of low conductivity is in fact always present just above the tropopause, and if so to determine at what heights it lies and whether it is uniform or patchy in nature. A series of such soundings might clarify many of the questions raised in the present examination of the convective hypothesis of the origin of such a layer. Such measurements would also shed light on the interesting suggestion (Holzer and Saxon, 1952) that a layer of minimum conductivity could be responsible for exaggerated surface field fluctuations far from active thunderstorms.

III. A Note on Erroneous Cloud Physical Applications of Raoult's Law

Abstract--It is pointed out briefly that an error has appeared persistently in the form of Raoult's law used in analyses of the lowering of the vapor tension of cloud drops due to the presence of dissolved solutes. The magnitude of this error is shown to become as great as 191 per cent when the solute is sodium chloride. Attention is called to the way in which this error was incorporated into an analysis of condensational growth of cloud drops by Howell.

1. Introduction

The purpose of this note is to call attention to an error which has appeared repeatedly in statements of Raoult's law in the meteorological literature and which has led to certain inaccuracies in at least one recent paper on cloud physics.

2. Raoult's law

When m' moles of a non-electrolyte are dissolved in m moles of water, the relationship between the vapor tension e' of the resulting solution and the vapor tension e of pure water is given by Raoult's law as

$$\frac{e' - e}{e} = -\frac{m'}{m' + m}, \qquad (1)$$

which may also be rewritten as

$$\frac{e'}{e} = \frac{m}{m' + m} \quad . \qquad (2)$$

Equation (2) states that the ratio of the vapor tension of the solution to the vapor tension of the pure solvent equals the mole-fraction of the solvent present in the solution. In so-called ideal solutions, the law is (by definition) exact at all concentrations, and in real solutions of non-electrolytes it holds to a good degree of approximation at low and moderate concentrations (Daniels, 1948).

When lowering of the vapor tension of a solution is due, on the other hand, to an electrolyte, equations (1) or (2) no longer apply because of dissociation of the solute. There is not at present unanimous agreement as to the exact nature of the solutes present in hygroscopic nuclei in the atmosphere, but the substances most frequently suggested as important (sea salts, nitrous acid, sulfuric acid) all have in common the property of dissociating into ions in solution and hence must give vapor tension reductions different from those predicted by (1) or (2), which apply only to non-electrolytes. Despite this fact, Raoult's law is given only as one or the other of the above equations by Haurwitz (1941), Lowell (1945), and again quite recently by Neuberger (1951). (It might also be noted that, in the last reference, the symbols corresponding to m and m' in (1) and (2) are incorrectly identified with the masses rather than with the numbers of moles of solute and solvent.) The same form of Raoult's law appears in the recently revised Smithsonian Meteorological Tables (List, 1951), and forms the incorrect basis for all of the equilibrium supersaturations over solution droplets tabulated on pp. 375-379 of those Tables.

For <u>electrolytes</u>, Raoult's law must be modified to the form

$$\frac{e' - e}{e} = - \frac{im'}{im' + m}, \qquad (3)$$

where i is a factor, often called the van't Hoff factor, which varies both with the chemical nature of the electrolyte and with the concentration of the solution. In the limit of infinitesimal concentration of the solute, i becomes simply the number of ions comprising one molecule of the solute (e.g., two for NaCl, three for $MgCl_2$).

3. The van't Hoff i factor

As the solute concentration increases from zero, the value of the van't Hoff factor first decreases, but then begins to rise again for moderate concentrations and, for most strong electrolytes, attains values in excess of the number of ions per molecule at concentrations near the saturation value. The latter effect is particularly marked in the cases of salts which characteristically form hydrates (e.g., $MgCl_2.6H_2O$). The Debye-Huckel theory of interionic attraction gives a fairly good explanation of the behavior of i near zero concentration where i decreases with increasing concentration (Daniels, 1948). At high concentrations it is believed that the clustering of the highly polar water molecules about the ions (particularly about the cations) ties up a large fraction of the total population of water molecules to decrease appreciably the number of water molecules escaping per second per unit area of surface of the solution, the latter thereby behaving as if there were an apparent ionic concentration greater than the actual value.

Since the variation of i with concentration is dependent upon the chemical nature of the solute in question, and since there is not yet complete agreement as to the nuclear substances operative under natural conditions, it would scarcely be in order here to undertake an exhaustive examination of the physical chemistry of any one nuclear substance or mixture. However, in order to show how Raoult's law should be treated for whatever solutes ultimately prove to be of chief importance in atmospheric condensation, the case of NaCl nuclei is considered here in somewhat more detail than has been done in the meteorological literature before. If sea salt nuclei should prove to be the main atmospheric nuclei, then since NaCl comprises some 77 per cent by weight of the mixture of salts present in sea water, the Raoult effect of that salt will be of primary interest, though $MgCl_2$, present to the extent of about 11 per cent, will have to be considered carefully because its property of forming a hexahydrate will make it a quite significant factor in the physical chemistry of sea-salt nuclei under conditions of low relative humidity.

It is possible to compute the van't Hoff factor as a function of molality for any given solute from the variation of the activity coefficient of that solute with molality (Moore, 1950). The great wealth of data on activity coefficients would justify this approach once there is clear evidence that some one substance is of dominant importance in atmospheric nucleation, but the method is quite tedious, involving as it does a numerical integration of the Gibbs-Duhem equation for each determination of i. As a more direct approach available in the case of NaCl whose effect on vapor tension has been determined experimentally over a wide range of concentrations, i-values have been computed here from the observed magnitudes of the reduced vapor tensions of solutions of NaCl. Tabulated values of this quantity are given by Washburn (1926) for a range of molality of 0.1 to 6.0 (a saturated NaCl solution is about 6.05 molal at atmospheric temperatures). Three additional values needed for the very low concentrations attained in the later phases of drop growth were taken from the measurements of Dieterici and of Smits reported by Roth and Scheel (1923).

Table 1. Values of the van't Hoff factor, i, for Aqueous solutions of NaCl of molality M.

M	Mole-fraction of NaCl	i
0.0+*	0.0+	2.00-
0.044	0.00080	1.96
0.070	0.00126	1.90
0.098	0.00177	1.86
0.1	0.0018	1.83
0.2	0.0036	1.82
0.4	0.0072	1.84
0.6	0.0108	1.85
0.8	0.0144	1.87
1.0	0.0180	1.89
2.0	0.0361	2.04
2.8	0.0505	2.19
5.0	0.0902	2.66
6.0	0.1083	2.91

* 0.0+ is used here to denote the limit of infinite dilution.

Table 1 shows the values of i computed from these observed data. It is to be noted that even at the minimum point, i equals 1.82, so the reduction of the vapor tension of a droplet containing a nucleus of NaCl is at least 82 per cent greater than the value implied by the erroneous form of Raoult's law given by Haurwitz (1941), Lovell (1945), Neuberger (1951), and List (1951). Note also that near saturation, i has become so large (due to solvation of the ions) that an error of 191 per cent is made if these ionic effects are neglected in calculating the Raoult effect. For the frequently accepted case of sea salt nuclei, the corresponding error would be noticeably larger at this high concentration because of the much more pronounced hydration of the magnesium ions.

4. Köhler curves for NaCl nuclei

That the forms of Raoult's law appearing in the literature cited are in need of correction is indicated by the fact that this error has been carried into the very valuable work of Howell (1949) on cloud drop growth. Curiously, the neglect of ionic effects seems to be an error appearing in the meterorological literature of just this country. Köhler (1936) in his work on the vapor tension of droplets assumed a constant ''dissociation factor'' (as defined for the now abandoned Arrhenius theory) of 0.75 for his assumed NaCl nuclei. Wright (1936) considered several chemical possibilities for his nuclei and used constant factors to correct for the effects of ionization. His statement that, "The hygroscopic factor...may vary with the concentration of the solution, particularly when the solution becomes very dilute and the phenomenon of dissociation occurs", raises some doubt, however, as to whether he held a correct view of the underlying physical chemistry of Raoult's law. Best (1951), in a recent paper on drop growth, merely employs Wright's constant correction for solute dissociation.

Using the values of the van't Hoff factor given in Table 1, (i.e., effectively using the experimental values from which Table 1 was derived), the equilibrium supersaturation over droplets containing various specified numbers of moles of NaCl were computed for comparison with Howell's values (presented by him as his Figure 1). Each Köhler curve corresponding to a given nuclear size was pushed down as a result of the correction of the Raoult's-law error made by Howell, and its peak value of critical supersaturation was moved towards a larger drop-size. The corrected values of peak supersaturation are only about three-fourths as large as those found by Howell (not to be confused, however, with the supersaturations found by Howell in the course of his numerical integrations of the drop-growth equation, for comments on which see below).

The important question arises: What effects on Howell's computed growth rates would follow from a corrected treatment of Raoult's law? In an attempt to answer this, the writer calculated, from Howell's paper, the parameters needed to evaluate the growth rates for several different nuclear sizes and then sought to compare these rates with those obtained with the incorrect form of Raoult's law.[1]

The degree of supersaturation, S in Howell's nomenclature, is a quantity which must be known before a calculation of growth rate can be made in any given case. By reading off the S-values from Howell's growth curves for various drop sizes and nuclear masses of interest, and using these to calculate corrected growth rates, apparent errors of from 25 per cent to 30 per cent in rates (at the points of maximum error) were found. However, this was a fallacious approach which overlooked the principal contribution of Howell's entire analysis, namely the treatment of S as a dependent variable in the growth equation. The degree of supersaturation is itself strongly influenced by the vapor tension of the drops (in reality, and also in Howell's admirable analysis of the growth problem), so to use Howell's supersaturations along with

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[1] It may be worth noting here for the benefit of readers concerned with the theory that there appears to be an error of algebraic sign in Howell's formulation of the compensated diffusion coefficient as well as a discrepant location of a factor of 2π in the asymptotic form of this coefficient for very small drops.

the corrected vapor tensions is not permissible since this would appreciably overestimate the error in the growth rates.

There seems to be no other way to determine exactly how far off Howell's growth rates may be than to redo his integrations. This would entail an amount of labor which would carry this note considerably beyond its intended scope, so no final assessment of the Raoult's law error in Howell's work is given here. However, from certain numerical-physical arguments, the writer is led to suspect that in the regions of most rapid drop growth, Howell's rates may be too low by about 10-15 per cent. If so, the later history of drop growth might be sensibly affected, since it is exactly at this stage of cloud formation that the peak supersaturation is determining the lower limiting size of nuclei (and hence the total number of nuclei) to be activated for rapid growth. For the region of growth beyond a few microns, dilution has proceeded so far that the entire Raoult effect vanishes; hence the latter phases of Howell's theoretical growth histories are not here in question except inasmuch as they may be affected by the peak supersaturation.

IV. The Shape and Aerodynamics of Large Raindrops

Abstract--The physical factors which might be expected to control the shape of large raindrops are surface tension, hydrostatic pressure, external aerodynamic pressure, electrostatic charge, and internal circulation. Each of these is examined quantitatively and the conclusion reached that only the first three play important roles in producing the deformation characteristic of large raindrops. By analyzing an actual drop photograph, the distribution of aerodynamic pressures is deduced and is shown to imply that separation in the airflow about a raindrop has significant effects on drop shape and on a number of physical processes occurring at the surfaces of falling raindrops.

1. Introduction

It has been known for over half a century that large raindrops do not possess the streamlined form popularly described as the "teardrop" shape. High-speed photographs (Flower, 1928; Edgerton, 1939; Blanchard 1950) reveal, instead, that a drop falling through the air exhibits a marked flattening on its lower surface and smoothly rounded curvature rather than conical taper on its upper surface. For an example, see Figure 1 here. This long-recognized peculiarity of large drops has never been adequately explained, and only very few attempts to elucidate this matter have even been undertaken.

Although J. J. Thomson made, in 1885, some observations on the shape of liquid drops moving through various fluids, the first serious attempt to examine the meteorological problem of the shape of large raindrops appears to have been made by Lenard (1904). Using a vertical airstream with water drops suspended freely therein, Lenard carried out a number of experiments on terminal velocities, deformation, and breakup. He noted that a finite time, somewhat greater than a tenth of a second, was required for a large drop to attain its equilibrium degree of deformation and suggested that this might be due to centrifugal distortion set up by internal circulations which, for inertial reasons, took a measurable amount of time to become established by the surface friction of the air rushing past the drop. To the present writer's

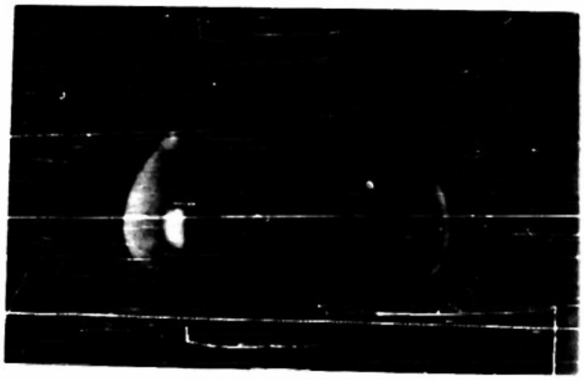

Figure 1. High-speed photograph of a large water drop falling at terminal velocity. Diameter of the drop calculated as a sphere is 6 mm, velocity of fall 8.8 m sec^{-1}, height of fall 12 m. Photograph by Dr. C. Magono, Hokkaido Imperial University; provided through the courtesy of Dr. U. Nakaya.

knowledge, no extension of this interesting beginning of the study of the drops shape problem was made during more than forty years following Lenard's work. Flower (1928), in a study of falling speeds had found it necessary to appeal to Lenard's theory of centrifugal distortion; and even when Laws (1941) carried out his very extensive measurements of the terminal velocity of water drops, no other theory of drop deformation was available to be invoked to account for the distortion of shape, and this despite the fact the reality of Lenard's postulated circulations had never been demonstrated.

Spilhaus (1948), in a short paper on raindrop shape and falling speed has made the only other contribution to this problem that has come to the writer's attention. Spilhaus suggested that the vertical flattening of large drops is due to the combined action of surface tension and aerodynamic pressures. Due to the deficit of external pressure around the waist of a drop, "the drop must deform so as to reduce the ratio of its area of cross section to perimeter in the vertical plane" in order to give the surface tension an opportunity to equilibrate the aerodynamic forces. Spilhaus may not have been aware of Lenard's earlier work, for he neither mentions it specifically nor gives any consideration to the centrifugal effects which Lenard held to be solely responsible for producing drop deformation. Neither Spilhaus nor Lenard offered any explanation of why large drops are not symmetrical about horizontal planes through their centers, and Spilhaus explicitly omitted this asymmetry from his theory in order to be able to use experimental data on drag coefficients of oblate ellipsoids. As will be pointed out below, Spilhaus used an incorrect relationship for determining the surface pressure increment due to surface tension and also erred in ignoring the significant effects of internal hydrostatic pressure gradients present in a drop falling at terminal velocity. With this background to the present problem, it seems appropriate to conclude that the issues involved are far from settled. In the present paper, some further contributions to this problem will be made and the results used to gain an improved understanding of some important features of the airflow about large raindrops.

2. Factors controlling raindrop shape

In the course of the present study an effort has been made not only to gain a better appreciation of the role of centrifugal distortion, surface tension, and aerodynamic pressures, but also to obtain a clearer recognition of the possible importance of electrostatic charges and internal hydrostatic pressure gradients.

The only reason that water drops can exist at all as mechanically stable systems is that surface forces at the water-air interface continually try to minimize the interfacial energy by tending to minimize the interfacial area. When this effect of surface tension acts alone, or nearly so, as in the case of cloud, drizzle, and even small raindrops, it succeeds in molding a drop into the shape characterized by minimum surface-to-volume ratio, i.e., a sphere. When, however, other factors than surface energy contribute significantly to the total energy of the drop, minimum total energy may be, and in fact is, inconsistent with perfectly spherical shape. One might hope to assemble all of these other energy factors, express mathematically their contributions to the total drop energy and then determine the equilibrium shape by minimizing the total energy with respect to some suitable shape parameter or parameters. If the gravitational effects (hydrostatic pressures) were the only additional energy factor, this might be done here just as it has been done (by tedious numerical processes) for the case of pendent and sessile drops (Adam , 1949). However, anyone fully cognizant of the difficulty of incorporating the aerodynamic factor into this type of approach will understand that the raindrop shape problem will probably never yield to any analysis which treats it as a classical minimal problem. Certainly this is so if that analysis is to be carried out by manual rather than electronic-computational means.

Recognizing this, the writer has sought to approach the problem simultaneously from two directions in order to converge ultimately upon a result (deduced aerodynamic pressure distribution) whose correctness may be judged tolerably well by comparison with certain experimental results in the fields of fluid dynamics and cloud physics. The central idea in this analysis has been to evaluate all of the factors controlling the pressure distribution inside a large drop and then, using certain surface physical concepts, to determine the surface pressure prevailing in the boundary layer just outside the drop surface. If the surface pressure pattern thus deduced is found to be in reasonably good agreement with aerodynamic principles (as will be shown to be the case), then some confidence may be placed in the theory of drop shape on which the calculations have been based. The logic of this approach will be further elaborated below.

Surface tension. Surface tension holds a rain drop together in the face of a number of tendencies to disperse the water contained in the drop. A consequence of the net inward attraction exerted on a surface molecule by the molecules lying deeper within the drop, this surface tension also produces an increase of pressure within the drop over and above that prevailing in the air outside. This increment in pressure, Δp_s, at a given point on the drop surface is given, in general, by

$$\Delta p_s = \gamma (1/R_1 + 1/R_2) \qquad (1)$$

where γ is the surface tension of the water-air interface and R_1 and R_2 are the principal radii of surface curvature at the point in question (Adam, 1949). The quantity Δp_s can be either positive or negative if one admits sufficiently arbitrary surface geometry. A principal radius will here be regarded as positive for the case where the water-air interface is convex as viewed from the air and Δp_s then becomes the difference between the water pressure just inside the drop minus the (aerodynamically controlled) air pressure just outside the interface at the point in question. It is to be noted that with these sign conventions, the principal radii are each everywhere positive (but not constant), and Δp_s is everywhere positive (but not constant) for a stable drop such as that pictured here in Figure 1. When, as here, both radii are of the same sign at each point, the surface is said to be everywhere synclastic. At a point where a general surface has radii of opposite signs, it is there anticlastic. During the processes of breakup of large, unstable drops the surface passes from the wholly synclastic over into a partially anticlastic form, as can be seen in photographs of artificially induced breakup taken by Blanchard (1950). An anticlastic surface can become dynamically unstable under certain conditions, but a synclastic surface cannot, as has been shown by Rayleigh and others (see, for example, Champion and Davy, 1936).'

In the special case of a spherical drop, $R_1 = R_2 = r$, where r is the drop radius, and then

$$p_s = \frac{2\gamma}{r}. \qquad (2)$$

This is the equation that was incorrectly applied by Spilhaus to his assumed ellipsoidal raindrop, using for r the radius of the circular cross section in a horizontal symmetry plane. Since this radius is only one of the two principal radii of curvature at a point on the waist of such a drop, and since the second principal radius is there smaller than the first, Spilhaus underestimated the pressure increment, particularly for his very large, and hence very much flattened drops. At the same time he neglected to consider the fact that the surface pressure increment is different, in general, at each different point of the drop surface, so his treatment of surface tension effects was doubly invalid in its details, even though acceptable in a qualitative sense.

Since γ for a water-air interface at OC is 75 dyne cm^{-1}, (2) reveals that a spherical drop of one millimeter radius must have, at that temperature, an internal pressure that is about 1500 dyne cm^{-2} above the external air pressure. For a drop of five millimeter radius, this increment would be only 300 dyne cm^{-2} if the drop could somehow remain spherical; and at the other extreme, for a cloud drop of five micron radius the internal pressure is some 300 millibars above the external air pressure. In the case of the cloud droplet, the pressure increment is so very large compared to hydrostatic pressure differences within the drop and to the minute aerodynamic pressures established at terminal velocity that each of these factors (and also all others) may safely be neglected in discussing drop shape. Hence cloud drops do simply assume the shape implying minimum surface free energy, thus accounting for their well known spherical form. But in the case of a raindrop at the upper end of the observed drop-size distribution, the surface pressure increments are only of the same order of magnitude as the pressure effects due to gravity and aerodynamic factors, so for this case, one must examine the shape problem more thoroughly.

The technique for determining, in general, R_1 and R_2 from a photograph of a falling drop will be explained below in Section 3.

Internal hydrostatic pressure. As a drop falls at its particular terminal velocity it is, by definition, no longer accelerating in the gravitational field. In a coordinate system moving with that falling drop, an observer would regard the drop as being just supported against gravity by the vertical components of the aerodynamic normal pressure forces and the surface shear stresses due to the apparently upward-rushing air. Consequently, there must exist within the drop a vertical pressure gradient of exactly the sort found in any mass of fluid at rest in a gravitational field. This hydrostatic pressure gradient appears to have been completely overlooked by both Lenard and Spilhaus, yet in the limit of very large raindrops the difference in hydrostatic pressure between top and bottom of a drop becomes quite important in controlling drop shape. Thus, for a drop of 5 mm radius (considered by Spilhaus, though, of course atypical of natural rain), this difference in hydrostatic pressure is about 1000 dyne cm^{-2}, or about three times larger than the surface pressure increment for a hypothetically spherical drop of this same radius. In the range of normal drop sizes, the hydrostatic effect is of course smaller, while the surface pressure contribution becomes larger: A drop of 1 mm radius has a top-to-bottom hydrostatic pressure difference of 200 dyne cm^{-2} as compared with its 1500 dyne cm^{-2} surface pressure increment.

If one could show that there exist appreciable internal circulations inside raindrops, then it would be necessary to take account of the dynamic pressure gradients that would inevitably be associated with these circulations. This point will be considered below. Here it will merely be noted, as a rather interesting point, that if raindrop shape were influenced only by surface tension and hydrostatic effects (with uniform external pressure), then the equilibrium shape would be one that was flattened on top and smoothly rounded below, i.e., just the reverse of the relative curvature observed in actual raindrops. This conclusion follows from the fact that the drop could then only be in equilibrium (internal pressures in hydrostatic balance) if the surface curvature were largest near the base and very small near the top, as suggested in Figure 2. In several photographs presented by Spells (1952), liquid drops falling very slowly through less dense liquids may be seen to possess exactly this sort of meridional profiles. The reason for this is, as will be shown later here, that at the low Reynolds numbers at which Spells' drops were falling, separation does not occur in the boundary layer and hence no dynamically low pressure can develop over the upper surface. The conclusion drawn here as to the shape a drop would possess if only surface tension and gravitational effects were involved, is sufficiently contradictory to the observed shape of large drops to imply clearly that other physical factors must play an important part in the morphology of raindrops.

Figure 2. Equilibrium shape of a falling liquid drop if only surface tension and hydrostatic pressure effects were significant. Observed shape of large raindrops is approximately that obtained by turning above shape upside down.

The way in which one may consider hydrostatic effects quantitatively in analyzing drop shape will be discussed below in Section 3.

Electrostatic charges. Since it is known that hydrometeors of all sizes ranging from cloud droplets up to the largest raindrops may carry electric charge, it is necessary to consider the possibility that the drop-shape problem might be sensibly affected by this factor.

By electrostatic standards the water in a natural raindrop is a good conductor. It can be shown (e.g., Jeans, 1941, p. 79) that a conductor carrying a local surface charge density σ experiences an outward-directed tension (negative pressure) whose magnitude per unit area is given by

$$T = 2\pi\sigma^2. \qquad (3)$$

This electrostatic tension opposes the surface tension and thus constitutes one of the several destabilizing factors that control drop morphology. This point assumes real interest as soon as one notes that on any conductor of variable surface curvature there is a tendency (counteracted only by external fields due to neighboring charged bodies) for the charge to distribute itself in such a manner that σ becomes largest where the surface curvature is largest. Hence as a charged raindrop began to flatten out due to aerodynamic effects, more of the total available charge would migrate towards the waist of the drop and would there produce a locally exaggerated suppression of the surface tension effect which serves to oppose the effect of low aerodynamic pressures near the waist. Consequently the drop would have to deform still more to increase the quantity $(1/R_1 + 1/R_2)$ around the waist in an effort to attain pressure equilibrium. This further flattening would then not only further decrease the external air pressure at the waist, due to continuity- and Bernoulli-effects in the airflow, but would at the same time have the additionally unfavorable effect of calling for still further buildup of surface charge density near the increasingly sharply curving waist. This would, in turn, oppose even more strongly the surface tension effects that are trying to hold the drop together, and so, until the drop became so flattened as to be torn apart by aerodynamic forces. This qualitative picture suggests so vividly and plausibly a mechanism for the breakup of large raindrops in thunderstorm precipitation currents that it is perhaps regrettable that it must next be shown that this interesting hypothesis is quantitatively tenable only for quite abnormal degrees of charging of the drops.

In the region just outside a point on the surface of a raindrop having local surface charge density σ, the electric field intensity is

$$E = 4\pi\sigma \, . \qquad (4)$$

Now the greatest possible value that σ can assume is given by (4) when E is set equal to E_d, the dielectric strength of the surrounding air. Any greater surface charge will induce corona discharge that will reduce E to E_d. E_d is pressure-dependent and is also sensitive to the geometry of the charged conductors involved, but for the cloud physical problem at hand, one will be conservative (in the sense of admitting rather high values of σ and hence of T) if he puts E_d = 30,000 volt cm^{-1} in (4), solves for the implied surface charge density, and then inserts this into (3) to determine the greatest value T can assume before corona discharge sets in. The result is

$$T_d = \frac{2\pi E_d^2}{(4\pi)^2} = \frac{E_d^2}{8\pi} = \frac{10^4}{8\pi} = 400 \text{ dyne cm}^{-2}$$

for the sea-level value $E_d = 30{,}000$ volt cm^{-1} = 100 e.s.u. At the 500 mb level, where E_d falls to about 15,000 volt cm^{-1}, T_d could be no greater than 100 dyne cm^{-2}.

These electrostatic effects (decrements of pressure on passing from the air side over into the water side of the drop surface) are of the order of magnitude of Δp_s for large drops as calculated roughly above, but they have been computed here for values of σ that appear to be substantially larger than any yet observed directly or indirectly. Thus a drop of 5 mm radius with so high a surface charge density as to imply $E = E_d$ at its surface would bear a total charge of $q_d = r^2 E_d = 0.25 \times 100 = 25$ e.s.u., at the earth's surface or about 12 e.s.u. at the 500 mb level. Gunn (1947, 1950), however, found by direct measurement from aircraft flying through precipitating clouds that drops seldom bear charges in excess of 0.1 e.s.u. Furthermore, his values were notable in that they are almost an order of magnitude greater than those previously reported for raindrop charges as measured at the earth's surface (Chalmers, 1949). Gunn (1949) has given an interesting possible explanation of why raindrops may not be able to accumulate charge to such a degree as to produce corona discharge of the type here tacitly assumed (isolated drops discharging into the air).

It would seem, then, that attractive as is the electrostatic factor in explaining drop shape and breakup, such observations as do exist emphasize its slight quantitative importance under normal circumstances. The electrostatic factor should, perhaps, be held in mind as possessing possible significance in processes occurring in the regions of highest electrical activity of thunderstorms, but elsewhere it may be ignored on the basis of existing drop-electrical measurements. It may be noted that in the regions of peak field strength within thunderclouds, the shape problem must also be considered in relation to the Macky effect due to external electric fields (Macky, 1931), but this case will not be treated in the present paper.

Internal circulations. Real fluid flow is fundamentally distinguished from perfect fluid flow by the fact that the former, but not theslatter, is characterized by the "condition of no slip" at surfaces bounding the region of flow. When the boundary is a solid, as in the case of flow over an airfoil, this condition implies that the air in contact with the boundary is at rest relative to that boundary. But when the boundary is the surface of a liquid, as in the case of a raindrop falling through the air, this condition can be satisfied even if the surface layer of air is slowly moving, for the interfacial liquid may be drifting downstream at some slow rate. In the case of a raindrop moving downward through air, any such surface circulation induced by shear stresses exerted by the ambient air would in turn induce some sort of axisymmetric internal circulation.

Lenard (1904) postulated the existence of such internal motions and regarded them as capable of accounting for the drop deformations which he had observed; but he made no attempt to demonstrate their reality experimentally nor to predict their intensity theoretically. Qualitatively, one can say that at least a very slow internal circulation is almost inevitable; for the dynamic boundary condition pertinent here is that of continuity of tangential shear stress across the water-air interface, and since water's viscosity is not infinite, at least a slight amount of internal motion seems certain to develop. In the analysis that will be given below in Section 3 it will be necessary to know whether the pressure at a point on the vertical axis of a drop is equal to that at a point at the same height above the base of the drop but lying just inside the drop surface. In view of the relatively small radii of curvature of the water-particle trajectories in any internal circulations, one can show that horizontal uniformity of pressure would be noticeably altered if surface water velocities of much over one-tenth the drop's falling speed can be developed. Consequently it becomes indispensable here to obtain an estimate of the intensity of the internal circulation.

Bond (1927) has examined theoretically the problem of internal circulations for the case of a liquid sphere moving through a dissimilar liquid medium for the case of Reynolds numbers in the Stokes law range, and has shown that a dimensionless quantity,

$$k = \frac{2\mu + 3\mu'}{3\mu + 3\mu'}$$

is a measure of the extent to which the drag law for a drop of liquid of dynamic viscosity μ' moving through a medium of viscosity μ departs from the drag law for a rigid sphere moving through the same medium. Since μ for air is about 1.7×10^{-4} poise at 0C, while μ' for water is about 170×10^{-4} poise at the same temperature, k is about 302/303 = 0.997 for the raindrop case, whereas it would be 1.000 for the case of a falling solid sphere. Hence for drop sizes whose terminal velocities lie within the Stokes law range, it appears that internal circulations must be relatively insignificant. However, for the sort of drops of primary interest here, the Reynolds numbers lie in the range from about 10^2 to 10^3 so Bond's criterion is not rigorously applicable to the present problem. Nonetheless, this part of Bond's analysis is of qualitative value here in that it calls attention to the fact that the development of internal circulations does not depend on just the external Reynolds number, but rather on the relative viscosity of the interior and the exterior fluids.

It is particularly necessary to keep this latter implication of Bond's work clearly in mind in examining a number of experimental studies recently carried out to determine, for chemical engineering reasons, the nature of the internal circulations occurring inside a heavy liquid drop falling through a lighter liquid (Garner, 1950; Spells, 1952). Circulations were readily observable photographically in these studies, but they all concerned situations wherein there was only a very slight difference in viscosity between the drop material and the external medium, while in the case of a raindrop falling through air the viscosity of the drop exceeds by two orders of magnitude that of the surrounding medium. Hence, one must note well that these recent studies do not bear very close relation to the raindrop problem.

Richardson (1950) has made some experimental studies of the breakup of water drops falling from a tower 125 feet high and has suggested that their breakup is due to the effects of internal circulation; but he appears to have obtained no direct evidence to support this view. He did observe that drops of a very viscous liquid (thickened methyl salicylate) resisted breakup far more effectively than did water drops, and argued that this was due to their resistance to the development of internal circulations. One must question this interpretation on the ground that the increased viscosity can, and indeed must, also play an important role in suppressing breakup by inhibiting the rapid oscillations that probably initiate breakup in oversize drops (Blanchard, 1950).

Blanchard (1949) attempted to observe internal circulations in water drops suspended in a vertical wind tunnel. He introduced fine particles of alumina into the drops to serve as tracers in revealing internal motions, but reported no evidence for any circulations. His observations may be inconclusive due to the fact that his tracer particles might have been too large ("300 microns and under") to be carried along in currents of the order of centimeters per second. Kinzer (unpublished) has observed very slow rolling motions inside drops containing fine talc particles, but he estimated the velocities involved to be less than a centimeter per second, which can be shown to be too slow to have appreciable centrifugal effect on drop shape.

Because of the importance of settling the question of whether internal circulations should be important in the drop-shape problem, the writer has sought a theoretical basis for estimating the upper limit to the circulation velocities that could develop within a large drop falling at the experimentally established limiting speed of about 8 m $\sec^{-1}$. The analysis is based upon the following assumptions:

(1) The shear stress is continuous across the water-air interface.

(2) The condition of no slip holds, but the interfacial molecules of water and air drift together so slowly downstream that as far as the external flow dynamics are concerned, the surface air molecules' speed may be assumed to be negligibly small compared to the relative airspeed at infinity (8 m $\sec^{-1}$).

(3) The drop remains spherical. A corollary to this assumption is the implication that the stream function inside the drop corresponds to that of a spherical vortex.

Any exception to assumption (1) would imply finite shear stress acting on an infinitesimal lamina of fluid, i.e., infinite accelerations would result from any failure for this condition to hold, so this first assumption is above reproach. That the surface air velocity at the base of the boundary layer may be regarded as zero compared to the falling speed of the drop (assumption (2)) is an assumption that can only be tested <u>a posteriori.</u> It will be shown below to be admissible. Assumption (3) is introduced to simplify the analysis even though it fails to hold in the case of interest here. However, departure from sphericity ought not have any large effect on the chances for development of internal circulation since the experimental work of Garner (1950) and Spells (1952) demonstrates that the type of vortices predicted by Bond (1927) appear in highly deformed drops of liquid in liquid. Assumption (3) simplifies the analysis primarily because of the corollary implication concerning the nature of the internal stream function. For a spherical drop the well known stream function for a spherical vortex may be used to determine the motion.

A stream function exists for simply kinematical reasons by virtue of the continuity equation, and so holds whether the motion is irrotational or, as here, rotational. The general form of the stream function ψ for any axisymmetric flow, when specialized to the case of motion within a sphere, reduces to the form

$$\psi = A(r^2 - a^2)r^2 \sin^2 \theta \qquad (5)$$

where A is a constant, a is the radius of the sphere, r is the radial coordinate measured from the center of the sphere, and θ is the meridional coordinate measured from a polar axis directed towards the pole of the sphere towards which fluid moves along the polar axis, see Figure 3 and Milne-Thomson (1949).

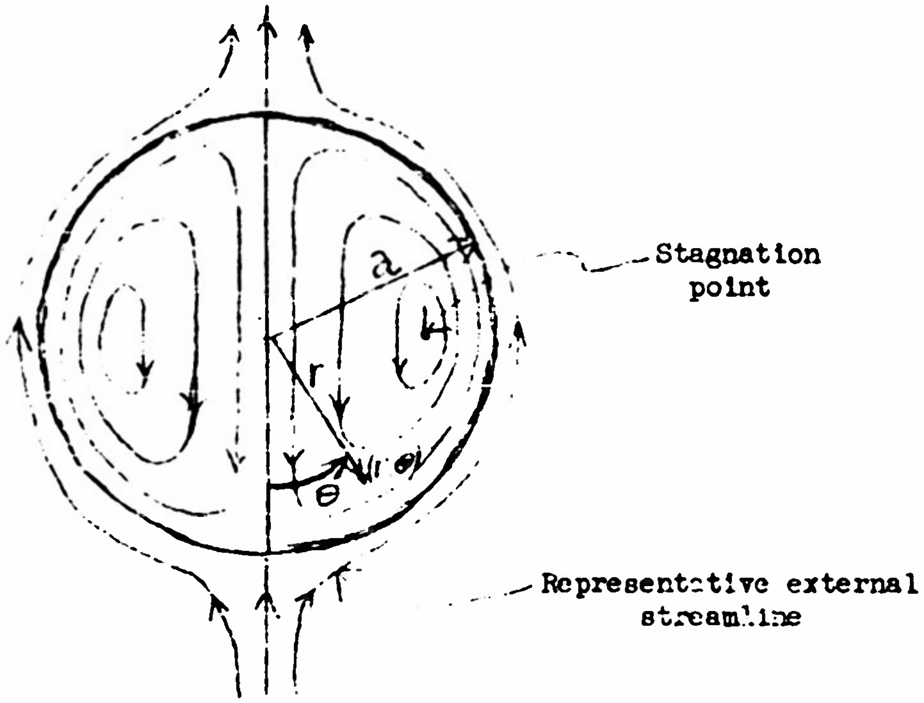

Figure 3. Definition sketch of vortical circulation inside a spherical drop.

The constant A in (5) assumes the value $3U_0/4a^2$ for a spherical vortex in a perfect fluid, where U_0 is the translation speed of the vortex center relative to the surrounding fluid, and assumes the value $\mu U_0/4a^2(\mu' + \mu)$ for a spherical vortex composed of a fluid of dynamic viscosity μ' moving very slowly through a fluid of dynamic viscosity μ (Bond, 1927). Due to the particular way in which (5) will be used here, it will be unnecessary to specify A (which is comforting inasmuch as the raindrop case corresponds neither to the perfect fluid limit nor to the low Reynolds numbers treated by Bond).

The meridional velocity u' at a general point r, θ is given by

$$u'(r,\theta) = \frac{1}{r}\left(\frac{\partial\psi}{\partial r}\right)_{r,\theta} = A\left(4r^2 - 2a^2\right)\sin\theta \qquad (6)$$

hence

$$u'(a, \pi/2) = 2a^2 A. \qquad (7)$$

Also, the velocity shear just inside the surface of the sphere at its waist is, from (6),

$$\left(\frac{\partial u'}{\partial r}\right)_{a,\pi/2} = 8aA \qquad (8)$$

so, combining (7) and (8) to eliminate A, it follows that

$$u'(a, \pi/2) = \frac{a}{4}\left(\frac{\partial u'}{\partial r}\right)_{a,\pi/2} \qquad (9)$$

and the problem of determining u' (a, $\pi/2$) becomes that of finding $\partial u'/\partial r$ at the same point. This can next be done with the aid of assumption (1).

Continuity of shear stress across the water-air interface requires

$$\mu'\left(\frac{\partial u'}{\partial r}\right)_a = \mu\left(\frac{\partial u}{\partial r}\right)_a$$

where the primed quantities refer, as before, to the water and the unprimed to air. Since $\mu' \simeq 10^2\mu$, one has

$$\left(\frac{\partial u'}{\partial r}\right)_a \gtrsim 10^{-2}\left(\frac{\partial u}{\partial r}\right)_a . \qquad (10)$$

The velocity shear in the boundary layer of air just outside the drop is of the order of u_1/δ where u_1 is the local air speed relative to the sphere at the outer limit of the laminar boundary layer and δ is that layer's radial thickness. Since outside of the boundary layer the flow at raindrop Reynolds numbers will be essentially potential flow at least up to about the waist of the drop, and furthermore since to assume potential flow is to be conservative here in the sense of admitting rather large waist velocities in the airflow, u_1 is taken as $1.5U_0$, where U_0 in the raindrop case is the terminal falling velocity. On the other hand, to evaluate δ, the boundary layer theory of Tomotika (1935) will be utilized. Tomotika showed that for a point at about 80° from the forward stagnation point of a sphere,

$$\delta \approx \frac{6.8}{u_1}\sqrt{2 U_0 \nu a} \qquad (11)$$

where ν is the kinematic viscosity of the air and a is the radius of the sphere. For $U_0 = 8$ m sec $^{-1}$ and a = 0.5 cm, δ is found from (6) to be about 0.05 cm. Hence, near the waist of such a large drop, $\partial u/\partial r \doteq u_1/\delta$ = 1200/0.05 sec^{-1} = 2.4×10^4 sec^{-1}, and then from (10) $\partial u'/\partial r \approx 240$ sec^{-1}.

Combining this last result with (9), one finds that $u'(a, \pi/2) \approx 30$ cm sec^{-1}. It is to be noted immediately that since this speed is less than 3 per cent of the air speed (12 m sec^{-1}) at the outer limit of the boundary layer near the waist of a drop falling at the maximum speed of about 8 m sec^{-1}, assumption (2) is rendered quite plausible a posteriori. If a similar calculation is carried out for the more probable value of 2.5 mm for the radius of a "large" drop, the circulation velocity at the waist is found to be only about 20 cm sec^{-1}.

The circulation intensity predicted by the above argument is substantially higher than that observed by Kinzer (in smaller drops), and it will become possible later in this paper to point out a very good reason why the actual circulations fail to reach the intensity just predicted. However, since this point will depend upon a deduction which hinges in part upon the negligibility of internal circulations, it is here necessary to proceed to show that even a surface motion of 30 cm sec^{-1} in a large drop will not lead to internal pressure gradients large enough to alter seriously the hydrostatic balance inside the drop. Consider the radially inward force that would develop as a centrifugal reaction to the here predicted vortical motion. The radii of curvature of the trajectories of particles moving just inside the boundary of a spherical vortex near its waist are nearly identical with the radius, a, of the vortex boundary, as may be seen in Figure 3. Since the speed of circulation falls off rapidly inward ($u' \propto r^2$) as one approaches the ring of stagnation points lying in an equatorial circle at 0.71a from the axis, and since furthermore the centrifugal reaction varies as the square of the circulation velocity, one will obtain a reasonable order of magnitude estimate of the centripetal force involved if he assumes that a lamina of radial thickness equal to about one-tenth of the distance from the surface to the stagnation point moves meridionally near the waist with the predicted speed of 30 cm sec^{-1} in a very large drop of 0.5 cm radius. The centripetal force per unit area acting on this lamina is found to be about 30 dyne cm^{-2}. This contribution to the internal pressure field is only 10 per cent of the surface tension contribution of about 300 dyne cm^{-2} for a drop of this size, and is a still smaller fraction of the hydrostatic pressure difference from top to bottom of such a drop. For a drop of 0.25 cm radius one finds that the centrifugal pressure effect represents a much smaller fraction of the surface tension incremental pressure. Hence it is concluded here that one may neglect internal circulation within falling raindrops as a first approximation, at least as far as such circulations might affect the shape of drops in the range of sizes now known to occur in natural rain. This conclusion will be strengthened in Section 4, when the phenomenon of separation is discussed.

Aerodynamic pressure distribution. In the writer's opinion, all of the factors capable of influencing drop shape, with the important exception of the aerodynamic factor, have now been considered. The next logical step for completing the drop-shape theory should thus be a direct evaluation of these aerodynamic pressure effects. Unfortunately, to carry out this last step would be extremely difficult. Without belaboring this fairly obvious point, it may be noted that the aerodynamic pressure distribution over the surface of a drop falling through the air is itself determined by the very shape one wishes to deduce. One could only proceed here, in principle, by some method of successive approximations in which each aerodynamic pressure calculation (based on the previous iterative approximation to the equilibrium shape) would be used to deduce a modified shape consistent with the surface tension and hydrostatic pressure requirements, and then this new shape would have to be used in the next iteration of the aerodynamic calculations, and so on. Difficult as this would be, one might be ready to attempt it were it not for the fact that there exists no general method for calculating analytically the pressure pattern about an arbitrary surface. The method of superposition of a suitable array of sources and sinks which is sometimes useful in treating the flow around revolutes is only sufficiently convergent to be practicable in the limit of very elongated revolutes such as dirigibles. To proceed with an iterative method in which each aerodynamic calculation had to be performed graphically or numerically was one course open to the writer; but he has instead chosen to proceed at this point upon a different tack: namely, to analyze a photograph of an actual drop of known size and falling speed in order to deduce these aerodynamic pressures which would be so difficult to calculate directly.

3. Calculation of aerodynamic surface pressures

On the basis of the discussions of drop morphology given in the preceding Section, the writer adopts the following hypothesis: The equilibrium shape of a large drop, bearing at most a charge small compared to the limiting value imposed by the dielectric strength of air and falling at terminal velocity, is that particular shape for which the joint action of the external aerodynamic pressures and the surface pressure increments just produce an internal pressure distribution that satisfies the hydrostatic equation within the drop.

This hypothesis has led the writer to employ the following method for calculating the aerodynamically developed external surface pressures: Given a photograph of a drop of known size and falling speed, one first calculates the stagnation pressure developed at the lower pole of the drop. It is fortunately one of the well established facts of fluid dynamics that regardless of almost all peculiarities of a given flow pattern about an object immersed in a fluid stream, the excess pressure developed at the leading stagnation point is $\frac{1}{2}\rho v^2$, where ρ is the fluid density and v is the speed of the fluid far from the object, measured relative to that object. Hence this first step involves no approximations. Next one measures, on the available photograph, the radius of curvature R_o of the drop surface profile at the lower stagnation point. For reasons of axial symmetry, $R_1 = R_2 = R_o$ at this point of the drop, i.e., the drop surface is locally a portion of a sphere of radius R_o at the stagnation point. Using this measured radius in (1) to compute Δp_s at the stagnation point, and adding the result to the computed stagnation pressure, one obtains the pressure prevailing just inside the drop at its lower pole. Next, using the hydrostatic equation, one may quickly determine the internal pressure $p_i(z)$ at any height z measured upwards along the vertical axis of symmetry from zero at the lower pole. Then, as long as internal circulations produce only negligible internal pressure gradients, the pressure just inside the drop surface at height z is equal to that already determined for the point along the axis at that height. Finally, if one can determine from the drop photograph the values $R_1(z)$ and $R_2(z)$, then (1) can be used to compute $\Delta p_s(z)$, and subtracting this from $p_i(z)$ yields $p_e(z)$, the external aerodynamically induced pressure at height z.[1]

From the preceding discussion it can be seen that the success of this method hinges upon being able to determine $R_1(z)$ and $R_2(z)$ from a single side-view photograph of a given drop. The technique for doing this turns out to

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[1] Note that all pressures represent algebraic excesses over the prevailing barometric pressure, and that the slight variation in the latter through the height interval spanned by the drop at any instant is ignorable because it is only of the order of 10^{-3} times the internal hydrostatic pressure variation in the same interval.

be quite straightforward.[2]

One of the two principal radii, say $R_1(z)$, is simply the radius of curvature of the meridional profile at the height z. This can be measured on a tracing made from an enlargement of a photograph of the vertical cross section, such as the one shown here in Figure 1. One constructs normals to the profile curve at each of a fairly dense series of points spaced regularly along the profile (the writer used a 45°-90° prism tangentometer in the determination of these normals) and from these the values of $R_1(z)$ can be determined by measuring the distance along the normal at z to the point of intersection with the normal drawn from the next adjoining point on the profile. In Figure 4 the distance R_1 for point P is shown as PC_1. By using an enlargement factor of about 20 and by using a fairly dense set of points (fifteen in all) along the profile, it was found to be easy to achieve precision of about 5 per cent in $R_1(z)$, as ascertained from repeated trials.

$R_2(z)$ is even more easily determined since this second principal radius, for a surface of revolution, can be shown[2] to be simply the distance from the profile point at z to the axis of revolution measured along the local normal to the profile at z. In Figure 4, R_2 is shown as the distance PC_2. The normals already constructed in the process of finding $R_1(z)$ facilitate rapid determination of $R_2(z)$.

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[2] The writer is indebted to Dr. J. M. Keller of the Department of Physics, Iowa State College, for examining and solving the problem in differential geometry that underlies the technique for determining the principal radii. His solution is too lengthy to be reproduced here and the writer knows of no published solution. However, subsequent to Dr. Keller's solving this problem, the writer came across a brief statement (Adam, 1949, p. 366) which agrees with his result and implies that the same problem has been treated previously.

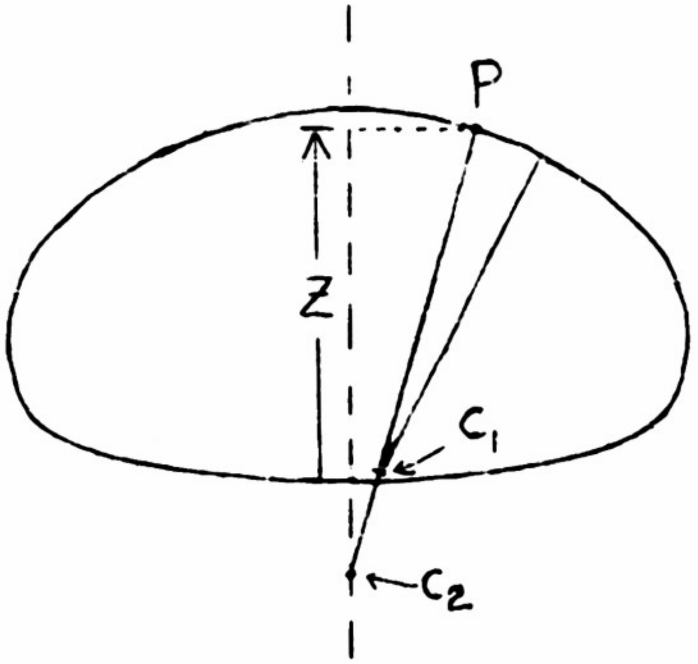

Figure 4. Determination of $R_1(z)$ and $R_2(z)$. For point P, $R_1(z) = PC_1$ and $R_2(z) = PC_2$.

Having established a method for determining $p_e(z)$, there remains only the question of availability of suitable photographs. Since it is obvious that satisfactory photographic results depend on using extremely high illuminations to permit exceedingly short exposure times (order of 10^{-5} sec), it is not entirely surprising that the writer has found virtually no existing photographs of either artificial or natural drops for which the falling speed and drop size are accurately determined. In fact, the writer has succeeded in obtaining only a single photograph fulfilling these requirements. This photograph, reproduced here as Figure 1, was taken by Dr. Choji Magono of the Hokkaido Imperial University, under conditions where both terminal velocity and drop volume could be measured. All of the remaining discussion is necessarily based upon this one photograph.

Since only the equivalent spherical diameter of the drop in Figure 1 was known, the exact distance scale on the photograph had to be determined preliminarily. On a tracing of an enlargement of the photograph the cross-sectional area of the drop was divided into a large number of horizontal strips of equal vertical width Δz. Next, for each such narrow strip, the radial distance r_i was measured from a point on the axis of revolution (midway between the upper and lower edges of the strip) out to the meridional profile curve. Then the quantities $\pi r_i^2 \Delta z$ were computed for each of the entire series of strips and their sum equated to the actual drop volume as given by Magono. From this equality, the scale-factor of the enlargement was ascertained for use in converting all subsequently measured distances on the photograph to true distances.

Proceeding in the manner now fully outlined, the writer determined $p_e(z)$ for Magono's drop. The results are presented in Figure 5. To aid in identifying the positions along the meridional profile where p_e assumes certain values of particular interest, five points (A to E) are labeled on the pressure curve and the locations of these points are indicated on the inset sketch of the drop profile. The lower stagnation point is subjected to an external pressure of 460 dyne cm^{-2} in excess of barometric pressure, but as the air accelerates in sweeping up and around the drop, the surface pressure falls, reaching a minimum of -590 dyne cm^{-2} near point C, just below the point of maximum horizontal cross-section. The pressures in the profile interval C-D are less accurately determined than those for other loci since here the profile's radius of curvature is changing quite rapidly and is very small. By performing the measurements in this region five times and averaging the results, the accepted values were found to deviate by about 10 per cent from their respective extremal values. As the air passes C the pressure very suddenly rises to a local maximum at D and then falls off again very slowly towards the upper pole at E, with a slight (and somewhat questionable) rise right at the pole.

If the airflow around this drop had been potential flow, the streamlines would have closed in above the drop in such a way that the pressure curve would have returned to positive values on the upper surface, ultimately

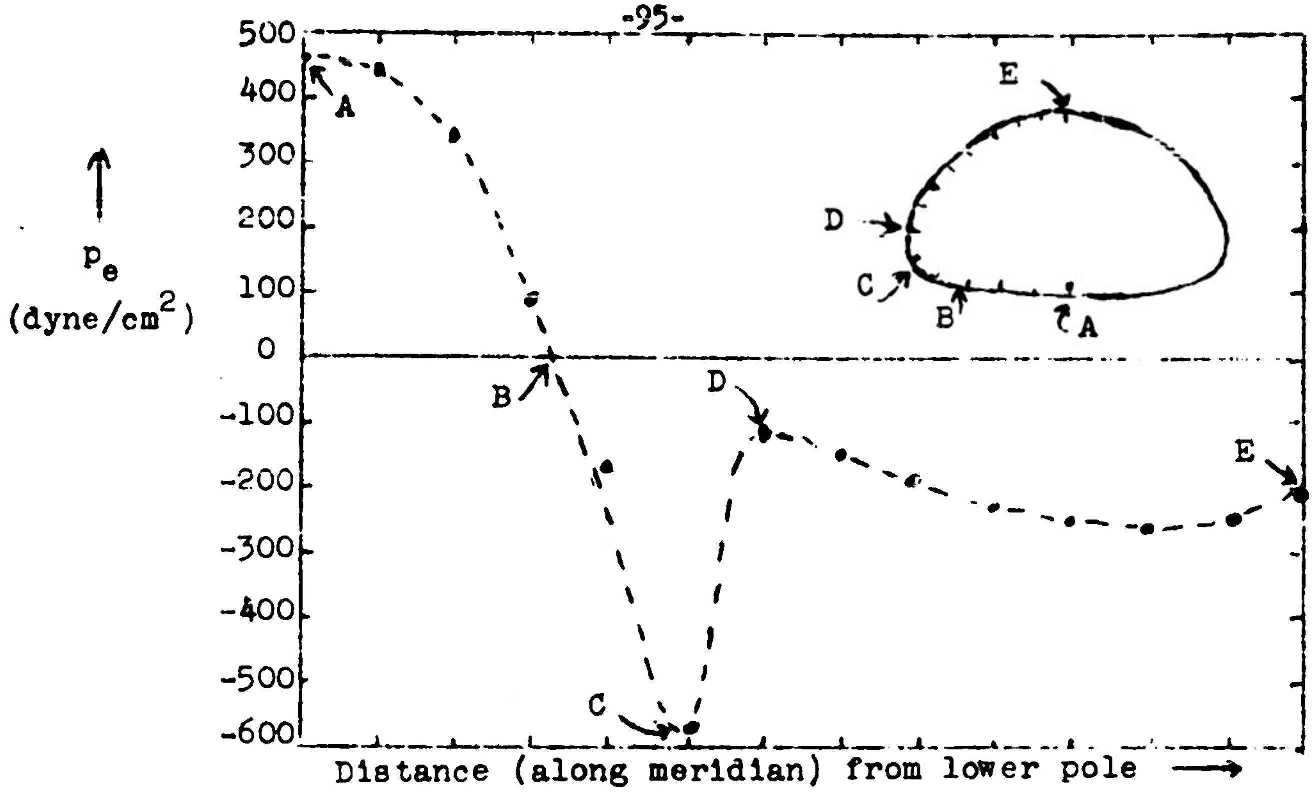

Figure 5. Aerodynamic pressure distribution deduced for Magono's drop (Figure 1). Letters refer to inset sketch.

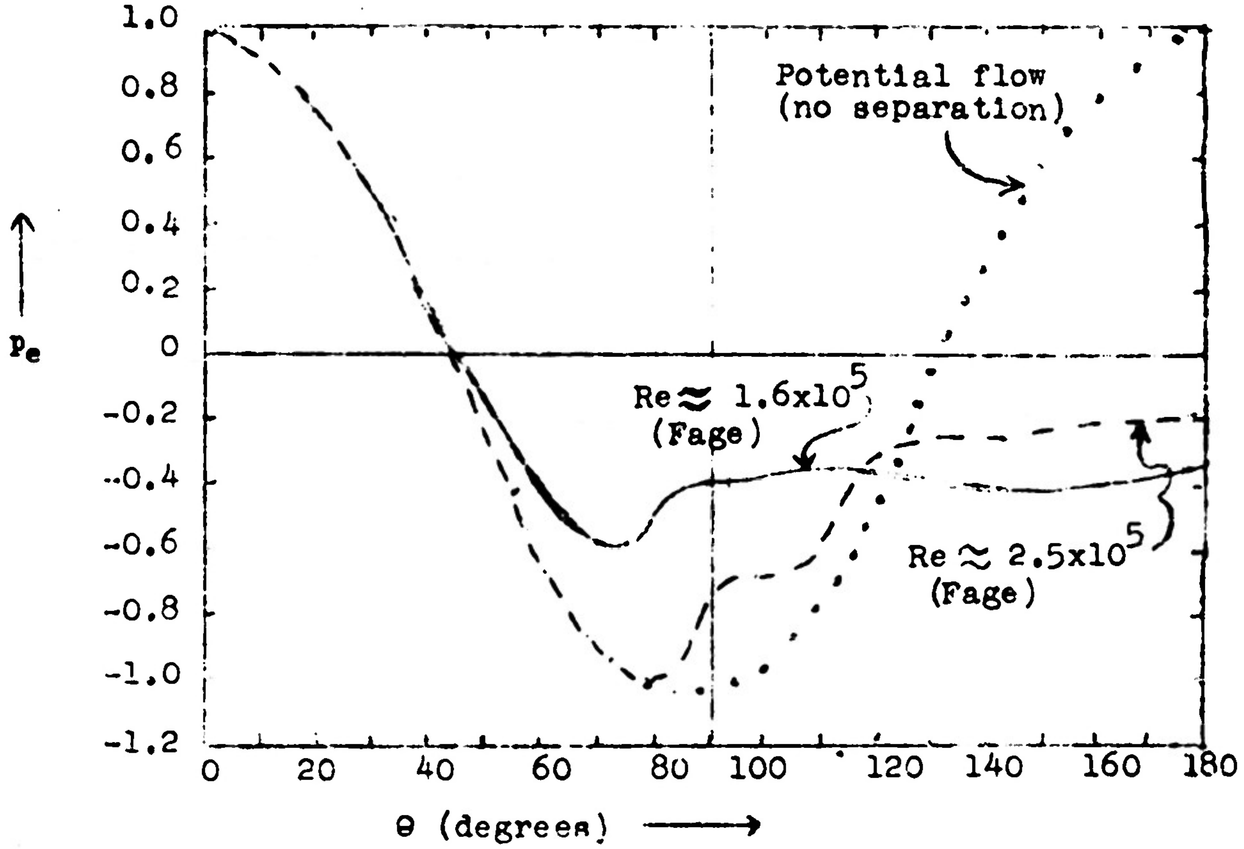

Figure 6. Aerodynamic pressure distribution around a sphere at $Re \simeq 1.6 \times 10^5$ and 2.5×10^5 after Fage. Dotted curve represents profile for the case of potential flow. Abscissa plotted in units of $\frac{1}{2} \varrho v^2$.

attaining a value of 460 dyne cm^{-2} at an upper stagnation point at E. That the pressures are, instead, found to remain negative (i.e., pressure less than barometric pressure) will be shown, in the next section, to imply that separation of the laminar boundary layer occurs in the flow around large raindrops.

4. Discussion of results

To review the logic of the present study, it must be noted that it has not been found possible here to predict the aerodynamic pressure effects on drop shape by proceeding directly from fundamental principles of fluid dynamics; instead the aerodynamic pressures have been deduced from the writer's hypothesis of drop shape. Therefore it follows that the test of the correctness of the shape hypothesis must involve a comparison between the results shown in Figure 5 and any available and pertinent experimental data.

It is understandable that the literature of experimental aerodynamics does not contain any data on observed pressure patterns around objects of raindrop shape since this is a quite unusual shape. Furthermore, it would not be easy to set about securing precisely the data desired because of the following considerations: If a "model" of a large raindrop were to be fabricated with an array of static pressure orifices distributed over its surface, the necessary internal tubing would probably preclude use of a model smaller than four or five centimeters in cross section, i.e., the model would have to be six or seven times larger than the prototype. To preserve dynamic similarity between model and prototype in the Reynolds sense, the experimental velocity could be only one-sixth or one-seventh of the prototype velocity of fall (about 8 m sec^{-1}) if air were used as the model medium; but at such low airspeeds, the uncertainties in measurement of the slight static pressure changes would pose rather serious obstacles to the success of the experiment. To use water as a medium can be seen to provide some little advantage, since the kinematic viscosity of water is only about one-tenth that of air but the density is about a thousand times that of air, so for given Reynolds number, the pressure effects would be ten times greater in water than in air. If any such model studies were to be undertaken, one would probably choose to use air, employ a conveniently large drop model, and then sacrifice dynamic similitude in order to get at least a rough notion of the behavior of the flow. The writer has not contemplated doing this himself, but the results would be of considerable interest.

In view of the lack of precisely the type of observational data needed for comparison with the present results, it becomes a next-best substitute to use data on spheres. Even for spheres one finds gap in the experimental results for Reynolds numbers lying between the upper limit of the Stokes law range and the lower limit of the region of critical Reynolds numbers for transition to a turbulent boundary layer. Drag data were found to be abundant for the entire range, but not surface pressure data. Thus it finally became necessary merely to look at pressure profiles for spheres at Reynolds numbers of the order of 10^5 (Fage, 1937), despite the fact that Magono's drop fell with a Reynolds number of only about 4×10^3.

Two of Fage's curves for the profile around a sphere (for $Re \approx 2.5 \times 10^5$ and $Re \approx 1.6 \times 10^5$) are plotted here in Figure 6. The similarities between these curves and that of Figure 5 are sufficient to provide considerable assurance that the present drop-shape hypothesis is at least fairly close to the truth. The pressures around the downstream hemisphere of Fage's sphere, like those deduced here for the upper surface of Magono's drop, fail to return to positive values (as do the pressures in potential flow, dotted curve of Figure 6) after starting to rise fairly rapidly just ahead of the region of maximum cross section. Now it is well known that this feature, in curves such as those of Figure 6, is due to the occurrence of separation in the boundary layer. At Reynolds numbers below those for which the boundary layer becomes turbulent ($Re \lesssim 4x10^5$) but above the Stokes law range ($Re \gtrsim 1$), the streamlines fail to close in downstream from the sphere and by this failure to create a downstream stagnation point the pressures remain low downstream from the zone of separation. Separation may be inhibited by fairing out the downstream portion of a body into a gently tapering form, but in bodies of large curvature aft (e.g., a deformed raindrop) separation is known to be easily established. The fact that the pressures deduced here for Magono's drop do exhibit this behavior may be regarded, then, as constituting fairly strong evidence in favor of the shape hypothesis used to determine these pressures. In still further support of this conclusion there exist two experimental observations on actual water drops which will next be shown to be quite consistent with the present deduction of separation in the airflow around large raindrops.

First, Gunn (1949) has reported a curious tendency for drops of one certain size (about 0.5 mm radius) to undergo marked sideslipping as they fall. Gunn has shown very convincingly that this must be due to a resonance phenomenon involving the natural frequency of mechanical oscillation of the drops and the frequency with which eddies are shed from the upper surface of the falling drop. Gunn invoked Moeller's (1938) extensive results on eddy frequencies for spheres to show that a sphere of 0.5 mm radius sheds eddies at a frequency of about 300 cps, almost exactly the natural frequency of ellipsoidal vibration of a water sphere of that size. Gunn's detection of this eddying phenomenon constitutes clear evidence of separation, since eddies can only be shed from a "deadwater" region bounded by a separating stream surface extending downstream from the given object. Furthermore, Gunn's observations concerned a drop-size much smaller than the one here analyzed; so at the much higher Reynolds number at which Magono's drop fell, separation should almost certainly be expected (and this the more so because of the sharper curvature on the upper surface of the larger and more flattened drop).

Second, Blanchard (1950) reported that when one drop of appropriate size is inserted into the airstream above another drop which is aerodynamically suspended in a vertical airstream, the upper descends upon the lower along a peculiar spiral path. Winny (1932) has, by means of photographs of the flow behind spheres at which separation was occurring, illustrated what appeared to be a spiral eddy pattern in the interval $Re \approx 2 \times 10^3$ to 8×10^3, so Blanchard's observations may be taken as further evidence for separation in the flow around water drops. A very complete discussion of the wake phenomena behind solid spheres has been given by Moeller (1938), who concluded that separation first appears at about $Re = 150$ and that periodic eddy detachment begins at about $Re = 450$ for solid spheres. For a somewhat deformed drops, these phenomena would be expected to appear at somewhat lower Reynolds numbers.

In all, there seems to be very good reason for believing that separation occurs in the airflow around all raindrops with diameters greater than about 0.5 - 1.0 mm. Since the present shape hypothesis has led to the deduction of a pressure profile of a type entirely different from that obtained with potential flow (see dotted curve, Figure 6) but quite similar to that characteristic of viscous flow at high Reynolds number (separating boundary layer), there would appear to be sufficient ground for accepting the shape hypothesis adopted here.

5. Implications of separation

It should be emphasized that the calculation of $p_e(z)$ for Magono's drop has interest not only in that it provides a check on the present theory of drop shape, but also in that it focuses attention on the phenomenon of separation itself. Gunn's (1949) observations imply that this phenomenon is already well established in flow about raindrops of modal size (1 mm diameter) falling at Reynolds numbers of less than 300, which finding is in good agreement with Moeller's work on solid spheres. Hence separation appears to be a phenomenon to be reckoned with in any theory of microphysical processes involving raindrops. The kinematics of ion deposition on falling raindrops, for example, must be admitted to be affected to some extent by the failure for simple potential flow to occur on the upper surfaces of drops. Analyses of heat and water vapor transfer to or from water drops must take separation into account. As Blanchard has found experimentally, the dynamics of a "fall-on" collision between two drops will be sensibly affected by the existence of a pulsatory wake set up behind a drop about which the flow is undergoing separation. Finally, the size-dependence of the terminal velocity of raindrops must be largely due to the well established effect of separation on form drag. For Reynolds numbers in the approximate interval 10^1 to 10^5, the drag coefficient of a sphere is nearly constant because in this range form drag (due to the presence of a deadwater region) rather than skin friction drag is of controlling importance, and separation produces a deadwater region whose dimensions remain roughly independent of Reynolds number until the latter reaches the critical transition value (meteorologically (unattainable for raindrops, which break up well below Re_c). Altogether, the effects due to separation, whose existence in raindrop aerodynamics seems quite clearly indicated, must constitute a significant factor in the physics of rain.

The detection of separation sheds further interesting light on the reasons for the probable non-existence of appreciable internal circulation inside raindrops. The skin-friction drag at the surface of a liquid drop about which the flow undergoes separation is markedly less favorable to the establishment of internal circulation of the spherical vortex type than is the skin-friction drag in the non-separating case. Starting from a zero value at the lower stagnation point, the downstream drag of air on water must reach its maximum value well forward of the separation point and then must fall once more to zero at the separation point where, by definition, there exists a zero radial velocity shear right at the drop surface (see Goldstein, 1938, and the suggested flow pattern of Figure 7). Then, downstream from the separation point,

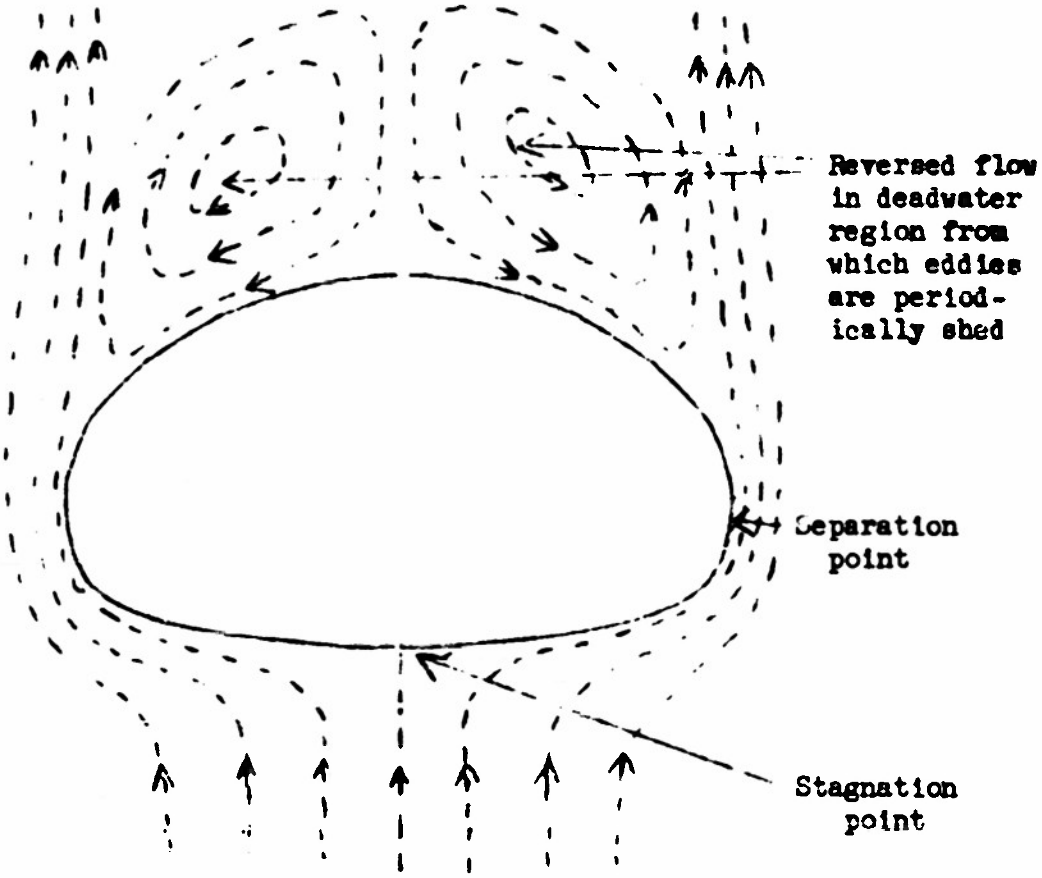

Figure 7. Suggested flow pattern around a large raindrop when separation occurs.

there will tend to exist a ring vortex of reversed circulation concentric with the symmetry axis of the drop. The presence of such a circulation over the upper portion of the drop surface will serve to cut down any incipient internal vortical circulations that do tend to become established by the drag forces acting over the lower surface of the drop. Hence, once one has recognized that separation is characteristic of the flow around raindrops, he has available a very strong basis for predicting that nothing like a spherical vortex of the Bond type will occur within large drops, for there simply does not exist a sustained downstream tugging of surface air on surfacewater over the entire surface of the drop. This argument could not, of course, logically be used earlier, since to assume separation from the start would be to postulate the very phenomenon whose theoretical deduction has here constituted the best available test of the working hypothesis for drop shape. Furthermore, at the time that the writer was still striving to settle the question of the existence or non-existence of internal circulations he was not yet aware of the experimental indications that separation occurs in the flow around drops. In the analysis of internal circulations carried out above (Section 2) a surface circulation speed of about 30 cm sec^{-1} was predicted. That this result is substantially too large to agree with the observations of Blanchard and of Kinzer is now understandable in retrospect, for in that analysis it was tacitly assumed that the surface air flow is favorable to generation of a vortical circulation everywhere over the surface of a drop. In reality, the opposing influences of frictional drag at lower and upper surfaces of a drop must be expected to prevent such strong circulation from developing.

Finally, it is to be noted that separation appears to be responsible for the asymmetry of a large raindrop with respect to a horizontal plane through its center. It was pointed out in Section 2 above that if only surface tension and hydrostatic pressure effects controlled drop shape, these would produce drops with rounded bottoms and rather flattened tops. However, because a stagnation point inevitably occurs at the lower pole, while one cannot develop at the upper pole because of separation of the boundary layer, it follows that the lower aerodynamic pressures over the upper surface demand an appreciable larger Δp_s there than on the underside, i.e., the curvature of the upper surface must be greater in order to satisfy the requirement of internal hydrostatic equilibrium in the face of the considerable aerodynamic pressure difference on upper and lower surfaces. Hence the drop becomes rounded on the top but flattened on the bottom, as revealed by photographs. This asymmetry of large drops, rather well accounted for on the present drop-shape hypothesis, was not explained by either Lenard (1904) nor Spilhaus (1948) in their studies of drop morphology.

6. Summary

A review of previous efforts to understand the peculiar deformation characteristic of large raindrops revealed that little has been done in the past to clarify this problem. The factors of surface tension, hydrostatic pressure gradients, external aerodynamic pressures, electrostatic charge, and internal circulations were examined quantitatively and only the first three of these were found to be significant in controlling drop shape. Adopting the hypothesis that the equilibrium shape of a raindrop falling at terminal velocity is that for which the aerodynamic pressures and the surface tension pressure increments conspire to just produce an internal pressure pattern satisfying the hydrostatic equation, it was found possible, by analyzing a single drop photograph to deduce the aerodynamic pressure profile along a meridian of the drop. This profile revealed clear evidence of separation of the laminar boundary layer in the airflow around the drop. Since separation effects could also be shown to exist in certain experimental observations, it has been concluded that the working hypothesis for drop shape has been successful in explaining the long-recognized deformation of large raindrops. A number of implications of separation were pointed out qualitatively, and it was noted that the distribution of skin-friction drag over the surface of a raindrop at which separation occurs is decidedly unfavorable to the generation of internal vortical circulation.

7. Suggestions for future research

That the writer has only succeeded in securing a single drop photograph suitable for the present type of analysis is regrettable. In the past, presumably, there has been little occasion for obtaining such difficult photographs under conditions where drop size and falling speed could be determined accurately. However, it now seems very desirable for the experimentalist to obtain a set of such photographs over the whole drop-size range of meteorological interest in order that a complete picture of the flow regions characteristic of the various drop sizes may be delineated by the method developed here. Such information should prove very useful in extending present theories of heat and vapor transfer to and from raindrops.

Secondly, since the present study is regarded by the writer as only a first step towards the more significant objective of understanding the breakup of large raindrops, he wishes to take this opportunity to urge extension of the sort of laboratory studies so well begun by Blanchard (1950). The wealth of intriguing questions raised by Blanchard's work and the light that could potentially be shed on the dynamics of drop breakup by further studies of this sort make a continuation of the research most desirable. In this connection, attention is called to a brief critical discussion of Blanchard's work by McDonald (1951), where a number of suggestions for improving this type of study have been offered.

Finally, it would still be desirable to have more conclusive experimental data on the intensities of internal circulation in water drops of various sizes. For drops just below the size for which separation first appears (probably around 0.5 mm diameter) it may be possible that circulation is actually better developed than for larger drops on whose upper surface a reversed flow develops.

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Dr. J. M. Keller's generous assistance in solving the basic problem in differential geometry which underlies the quantitative analysis of drop

photographs has greatly contributed to the work reported here. The writer also acknowledges the aid of Dr. Choji Magono of the Hokkaido Imperial University whose photograph provided the observational datum for this present analysis. He also wishes to thank Dr. U. Nakaya, now of the Snow, Ice, and Permafrost Research Establishment, for his assistance in making this photograph available.

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