The rate of evaporation of droplets.

Evaporation and diffusion coefficients, and vapour pressures of dibutyl phthalate and butyl stearate

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The rate of evaporation of drops of dibutyl phthalate and butyl stearate of radius approx. 0.5 mm. has been studied by means of a microbalance over a range of atmospheric pressures down to approx. 0.1 mm. of mercury. Wide departures from Langmuir’s evaporation formula were found to occur at these low pressures, but results are in good accordance with the theory of droplet evaporation advanced by Fuchs which hitherto has not been tested experimentally. This experimental verification of Fuch’s theory for droplets of medium size evaporating at low pressures shows that the theory can be applied to the evaporation of very small drops at atmospheric pressure. The vapour pressures of the above liquids have been measured by Knudsen’s method and the evaporation and diffusion coefficients calculated from the experimental data.

List of symbols used

\( a \) = radius of drop.
\( A \) = collision area for ‘air molecule’ and diffusing molecule
\( A_1, A_2 \) = areas of holes in vapour-pressure experiment.
\( \alpha \) = evaporation coefficient.
\( \alpha_{12} \) = factor to allow for persistence of velocities.
\( c \) = concentration of vapour at wall.
\( c_0 \) = concentration of vapour at saturation.
\( c_1 \) = concentration of vapour at distance \( A \) from drop surface.
\( D \) = diffusion coefficient at air pressure \( P; D = Y/P \).
\( \lambda \) = distance from surface of drop to region of concentration \( c_1 = kT/\lambda P \).
\( H \) = \( \alpha vP/Y \).
\( k \) = gas constant per molecule.
\( k_1, k_2 \) = constants in Knudsen’s equation (see equations (27), (29)).
\( L \) = \( \alpha v_0 m_2/\rho \).
\( L_1 \) = length of tube in vapour-pressure experiment.
\( \lambda_2 \) = mean free path of a diffusing molecule.
\( m_1 \) = mass of ‘air molecule’.
\( m_2 \) = mass of diffusing molecule.
\( m \) = mass of droplet.
\( M \) = molecular weight.
\( \nu \) = \((kT/2\pi m_2)^{1/2}\).
\( p \) = pressure of vapour.
\( p_0 \) = pressure of vapour at saturation over drop.
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\[ p_\infty = \text{pressure of vapour at saturation over a plane surface.} \]
\[ p_1 = c_1 kT. \]
\[ P = \text{pressure of air.} \]
\[ q = \frac{ds}{dt}. \]
\[ q_0 = \frac{ds}{dt} \text{ for portion of graph of } \frac{ds}{dt} \text{ versus } \frac{1}{P} \text{ which is linear.} \]
\[ r = \text{radial distance from droplet centre.} \]
\[ r_0 = \text{distance of charcoal from droplet centre.} \]
\[ R = \text{gas const. per g.mol.} \]
\[ R_1 R_2 = \text{radii of openings in vapour-pressure experiment.} \]
\[ \rho = \text{density of evaporating liquid.} \]
\[ S_{12} = \text{sum of radii of air molecule and diffusing molecule.} \]
\[ s = \text{surface of drop.} \]
\[ S_0 = \text{surface of drop at zero time.} \]
\[ \sigma = \text{surface tension of liquid.} \]
\[ T = \text{absolute temperature.} \]
\[ t = \text{time.} \]
\[ u = \text{velocity with which molecules leave the droplet surface.} \]
\[ W = \text{average } Y, \]
\[ W_1 W_2 = \text{weights of liquid lost by evaporation in vapour-pressure experiment.} \]
\[ x = \text{constant to allow for tube resistance in vapour-pressure experiment.} \]
\[ Y = DP. \]

I. Introduction

It is well known that small spheres of liquid evaporate in air in such a manner that the rate of change of surface with time is constant, a result which, as Langmuir (1918) showed, follows directly from Stephan's theory of diffusion. The expression

\[ -\frac{ds}{dt} = 8\pi D m_2 c_0 / \rho \tag{1} \]

(where \( s = \text{surface, } t = \text{time, } D = \text{diffusion coefficient, } c_0 = \text{concentration in the saturated vapour, } m_2 = \text{mass of a diffusing molecule, and } \rho = \text{density of the liquid} \)) has been verified experimentally for droplets varying in radius from a few millimetres to about 0.1 mm., and tested for a number of liquids of varying vapour pressure. It has also been tested, though less rigorously, on much smaller droplets in the size range \( 2 \times 10^{-4} \) to \( 5 \times 10^{-5} \) cm. by observing their rates of fall through air at atmospheric pressure. For these small spheres high-boiling organic substances were used, so that evaporation took place at a sufficiently low rate for measurement, and the interesting observation was made that the graph of \( s \) against \( t \), instead of being linear, curved slightly away from the time axis, the curvature being more marked the smaller the particle. It was clear that evaporation of these small droplets showed a progressive diminution in rate (expressed as \(-\frac{ds}{dt}\)) as smaller dimensions were reached. At the time this behaviour was attributed to the presence of non-volatile impurities, but in the light of recent work it seems likely that it really
represents the normal course of evaporation of spheres of these sizes. Unfortunately, on account of experimental difficulties, the experiments were not repeated and a study of still smaller droplets which should have shown a greater deviation proved still more difficult on account of increasing Brownian movement (Whytlaw-Gray & Patterson 1932, p. 169).

In addition, experiments have been made in these laboratories on the evaporation in air, at various pressures down to about 1 cm. of mercury, of droplets of about 1 mm. radius, and it was observed that whilst at any one pressure \( \frac{ds}{dt} \) remained constant its magnitude varied inversely as the pressure \( (P) \), a result in conformity with the diffusion theory, since \( D \) is proportional to \( \frac{1}{P} \). It is, however, clear that \( \frac{ds}{dt} \) cannot increase indefinitely with falling pressure, for evaporation can never exceed the vacuum rate; \( \frac{ds}{dt} \) must therefore approach asymptotically the rate of evaporation in a perfect vacuum as the air pressure becomes smaller and smaller.

Similarly, for droplets evaporating in air at atmospheric pressure, there must be a limiting size below which the rate of evaporation ceases to follow the simple expression, for, if it were not so, the number of molecules escaping per unit area from a very small droplet would exceed the number escaping into a vacuum, which is obviously impossible. This follows from Langmuir's formula

\[
-\frac{dm}{dt} = 4\pi a D c_0 m_2,
\]

where \( a \) is the radius and \( m \) the mass of the drop. Hence the loss per unit area per second is \( D c_0 m_2/a \), which approaches \( \infty \) as \( a \) approaches zero. It is hence clear that Langmuir's simple expression cannot be valid either for the evaporation of very small droplets at atmospheric pressure or for larger droplets at very low pressures. It is, however, reliable for droplets down to \( 10^{-3} \) cm. radius in normal air, and the deviations even at \( 10^{-4} \) cm. radius are small. At lower pressures for the larger drops the departure of \( \frac{ds}{dt} \) from constancy is inconsiderable down to about 1 cm. of mercury.

The theoretical aspect of droplet evaporation has been discussed by Fuchs (1934). Fuchs regards the diffusion process as not starting directly at the surface of the evaporating sphere of radius \( a \) but from the surface of an enveloping sphere of radius \( a + A \), where \( A \) is of the order of the mean free path of the air molecules. Very few air molecules will then be present in the spherical shell of thickness \( A \), which is substantially a vacuous space. The effect of this space will be negligibly small for larger droplets, but when \( a \) approaches \( A \) in magnitude the rate of evaporation expressed as \( -\frac{ds}{dt} \) will be decreased. Starting from this conception, Fuchs developed equations for the rate of evaporation of very small spheres but was unable to check them on account of the paucity of experimental data.

The present report presents a more complete treatment of the theory of evaporating droplets and describes experimental work carried out in order to throw light on the course of evaporation of very small liquid spheres. Since the direct study of
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small droplets is impracticable, we have had recourse to observations on comparatively large drops (ca. 0.5 mm. radius) at low pressures. Our treatment of the theory shows that information so gained is directly applicable to the calculation of the evaporation of very small droplets at atmospheric pressure.

II. Theoretical

(a) The general evaporation equation: drop in an infinite enclosure

Following the treatment of Fuchs we suppose that the concentration of vapour at a distance \( a + \Delta \) from the centre of the drop is \( c_1 \) molecules per c.c., a value less than the equilibrium concentration \( c_0 \), as will be seen below; \( \Delta \) is, of course, an equivalent distance, since actually there must be a concentration gradient within the spherical shell of radii \( a \) and \( a + \Delta \). The drop is imagined to evaporate in a gas at pressure \( P \) into an infinite space.

If the evaporation or accommodation coefficient is \( \alpha \), i.e. a fraction \( \alpha \) of the molecules which hit the surface condense, then the rate of evaporation into a vacuum is \( 4\pi \alpha \nu c_0 \) molecules per second, where \( \nu = (kT/2\pi m_2) \), \( k \) being the gas constant per molecule, \( T \) the absolute temperature, and \( m_2 \) the mass of the evaporating molecule. Hence the rate at which molecules arrive at the shell surface, distant \( a + \Delta \) from the droplet centre, is \( 4\pi \alpha \nu \Delta \) \( c_0 - c_1 \). This may be equated to the rate at which molecules leave by diffusion, in the steady state, or

\[
4\pi \alpha \nu \Delta \frac{c_0 - c_1}{c_0} = 4\pi (a + \Delta) D c_1,
\]

where \( D \) is the diffusion coefficient at the pressure \( P \). Hence

\[
c_1[(a + \Delta) D + a^2 \nu \alpha] = c_0 a^2 \nu \alpha,
\]
giving an evaporation rate

\[
-\frac{dm}{dt} = 4\pi (a + \Delta) \frac{D c_0 a^2 \nu \alpha m_2}{(a + \Delta) D + a^2 \nu \alpha},
\]

where \( m \) is the mass of the drop, or

\[
-\frac{dm}{dt} = \frac{4\pi \alpha D c_0 m_2}{D/(a \nu \alpha) + a/(a + \Delta)},
\]

Fuchs left the evaluation of \( \Delta \) in an indefinite form, but a sufficiently accurate result is easily derived. Let the collision area for the impact of evaporating and air molecules be \( A \), i.e. \( A \) is a mean value for the constituents of air. Let the velocity with which the diffusing molecules leave the droplet be \( u \), in general greater than the mean thermal value. The number of collisions is \( u(A P/kT) \) per second, the time between collisions \( kT/AuP \), and the distance between collisions

\[
(kT/AuP) u = kT/AP = \Delta,
\]
i.e. a molecule after leaving the droplet travels a distance \( \Delta \) before a collision occurs.
Since \( \lambda \), the mean free path of evaporating molecules, is given by
\[
\lambda = \left( \frac{m_1}{m_1 + m_2} \right)^{\frac{1}{2}} \frac{kT}{\pi P S_{12}^2},
\]
where \( m_1 \) is the mean mass of an air molecule, \( S_{12} \) the sum of the radii of evaporating and 'air molecules', and the concentration of evaporating molecules is neglected, then
\[
\frac{\Delta}{\lambda} = \left( \frac{m_1 + m_2}{m_1} \right)^{\frac{1}{2}} \frac{\pi S_{12}^2}{A} = \left( \frac{m_1 + m_2}{m_1} \right)^{\frac{1}{2}}.
\]

It should be noted that, unlike Langmuir's simple expression, equation (3) gives the correct rate of evaporation into a vacuum for drops of radius of the order 1 mm. For then \( \Delta \) is large compared with \( a \) and \( a/(a + \Delta) \) vanishes. Hence
\[
- \frac{dm}{dt} = 4\pi a^2 v x c_0 m_2,
\]
i.e. the correct value for \( a = 1 \) mm. and \( P = 0 \).

On the other hand, Langmuir's expression is reproduced under the conditions for which it holds, i.e. \( a \) of the order 1 mm. and \( P = 1 \) atm. Then \( a/(a + \Delta) \) becomes nearly unity and \( D/(ax) \) is negligible compared with unity, if \( a \) is mm., \( D \) approx. 0.1, \( x \) approx. unity and \( T = 20^\circ \) C, taking a molecular weight of the order 100.

It is clear, however, that \( D/(ax) \) will not be small compared with unity if either \( a \) or \( x \) is small. Considering only the variation in \( a \) at constant \( P \) and constant \( D \), equation (3) gives for the rate of evaporation per unit area
\[
- \frac{dm}{dt} \text{ (per unit area)} = \frac{D c_0 m_2}{D} \frac{a^2}{\nu x + a + \Delta}
\]
\[
= v c_0 a m_2 \quad \text{if} \quad a \quad \text{is very small}.
\]

This is the vacuum rate, and it follows, therefore, that the rate of evaporation of very small drops at atmospheric pressure is, per unit area, nearly equal to the rate of evaporation of unit area into a vacuum. This is clearly a remarkable and important result. As already mentioned, Langmuir's expression gives for the rate of evaporation per unit area \( - \frac{dm}{dt} \text{ (per unit area)} = D c_0 m_2/a \), i.e. infinite values as \( a \to 0 \). Fuchs's theory therefore gives evaporation rates per unit area at gas pressure \( P \) less than those given by Langmuir, but greater than those calculated for a plane sq.cm. evaporating into gas at pressure \( P \).

Clearly, equally great departures from Langmuir's result would be expected if the evaporation coefficient were very small, for then \( D/\nu x a \) would be large compared with \( a^2/(a + \Delta) \) even when \( a = 1 \) mm. and \( P = 1 \) atm. This is not likely to occur, however, with pure liquids.

These results are summarized in table 1, which contrasts the results of Fuchs
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### Table 1

<table>
<thead>
<tr>
<th>Equation due to</th>
<th>Decreasing radius ((a)) at constant pressure</th>
<th>Decreasing pressure ((P)) at constant radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(-\frac{dm}{dt}) (\frac{1}{4\pi a^2}) (\frac{Dc_0 m_2}{a}) (-\frac{ds}{dt}) (\frac{8\pi D m_2 c_0}{\rho}) (\frac{Y c_0 m_2}{\alpha P}) (-\frac{P}{\rho}) (\frac{1}{Y(a+\Delta)})</td>
<td>(-\frac{dm}{dt}) (\frac{1}{4\pi a^2}) (\frac{Dc_0 m_2}{a}) (-\frac{ds}{dt}) (\frac{8\pi D m_2 c_0}{\rho}) (\frac{Y c_0 m_2}{\alpha P}) (-\frac{P}{\rho}) (\frac{1}{Y(a+\Delta)})</td>
</tr>
<tr>
<td>Fuchs</td>
<td>(\frac{4\pi a Dc_0 m_2}{a + \Delta}) (-\frac{1}{a + \Delta}) (\frac{Dc_0 m_2}{a}) (-\frac{ds}{dt}) (\frac{8\pi D m_2 c_0}{\rho}) (\frac{Y c_0 m_2}{\alpha P}) (-\frac{P}{\rho}) (\frac{1}{Y(a+\Delta)})</td>
<td>(\frac{4\pi a Y c_0 m_2}{P}) (-\frac{1}{P}) (\frac{Y c_0 m_2}{\alpha P}) (-\frac{ds}{dt}) (\frac{8\pi Y c_0 m_2}{\rho}) (\frac{Y c_0 m_2}{\alpha P}) (-\frac{P}{\rho}) (\frac{1}{Y(a+\Delta)})</td>
</tr>
</tbody>
</table>

\(c_0, m_2, a, \Delta, D, \alpha, Y, \rho, \) and \(\rho \) are constants. The vacuum rate is calculated when \(a \to 0\) or \(P \to 0\).
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and Langmuir under various conditions. Fuch’s equation may be transformed to give the rate of change of surface with time in the form

$$-\frac{ds}{dt} = \frac{8\pi D m_2 c_0}{\rho} \left( \frac{1}{D a + \frac{1}{a + A}} \right).$$

(4)

The diffusion coefficient $D$ is inversely proportional to the pressure, i.e. $D = \frac{Y}{P}$, where $Y$ is a constant.

(b) The theory of evaporation in a finite vessel with absorbent walls

It now remains to study the evaporation of droplets under the conditions used in the experiment, in which a droplet is suspended inside an enclosure, the walls of which consist of an absorbent material such as charcoal, giving effectively zero vapour pressure at the walls. It is considered that the equilibrium pressure over the charcoal is roughly the same as that over the evaporating substance in the solid state at some temperature below the melting point, and owing to the large temperature coefficient of vapour pressure of the liquids used the vapour pressure at the walls is effectively zero. First let us derive Langmuir’s result under experimental conditions, and then consider modifications.

(i) From simple diffusion theory, neglecting Fuchs’s correction for the moment,

$$\frac{dm}{dt} = 4\pi r^2 D m_2 \frac{dc}{dr},$$

where $c$ is the concentration in molecules per c.c. at a distance $r$ from the drop centre.

If the last equation is written in the form

$$\frac{1}{4\pi r^2} \frac{dm}{dt} = \frac{D m_2 c_0}{r},$$

and integrated,

$$\frac{dm}{dt} \left( \frac{1}{a} - \frac{1}{r_0} \right) = 4\pi D m_2 c_0,$$

where the concentration is zero at a distance $r_0$ from the drop centre, and $a$ is the droplet radius; it is assumed that the slight variation in total pressure from the droplet surface to the wall does not affect the diffusion coefficient $D$, which is therefore regarded as a constant during the integration. It is also assumed that the mass of vapour passing through every spherical surface in unit time is independent of the radius of the surface, i.e. that the steady state is reached. In experimental practice the enclosure quickly fills with vapour at a graded concentration, and the steady state is achieved in a short time. Moreover, put $p_0 = c_0 kT$, since $p_0$ is usually small.

If $r_0 = \infty$ equation (5) may be written

$$-4\pi \rho \frac{da}{dt} = \frac{4\pi D m_2 p_0}{kT},$$

i.e.

$$-\frac{ds}{dt} = \frac{8\pi D m_2 p_0}{\rho kT},$$

(6)

which is Langmuir’s result. It follows, therefore, that Langmuir’s formula is not strictly true with a finite enclosure. The direct integration of equation (5) gives

$$\frac{a^2}{2} - \frac{a^3}{3r_0} = -\frac{D m_2 p_0 t}{kT \rho} + \frac{a_0^2}{2} - \frac{a_0^3}{3r_0},$$

(7)
where $a = a_0$ when $t = 0$. Hence it is not quite true to say that the rate of change of surface with time is constant. In many experiments, however, $a$ changes only slightly with time during the run, and thus

$$\frac{-1}{a} \left( \frac{dm}{dt} \right) = \frac{r_0}{r_0 - a} \frac{4\pi Dm_2p_0}{kT},$$

or

$$s = \frac{-8\pi Dm_2p_0 t}{\rho kT \left( 1 - \frac{a}{r_0} \right)} + s_0.$$  

This equation is identical with that due to Langmuir, except for the introduction of a factor \( \left( \frac{1}{1 - \frac{a}{r_0}} \right) \). When $a$ is increased to infinity, and $r_0 - a$ kept constant, then the correct expression for a plane surface for $dm/dt$ per unit area is reproduced.

(ii) Now consider how these equations which apply to experimental conditions are modified by the conceptions of Fuchs.

When Fuchs’s correction is introduced then, instead of equation (5), it is seen that

$$\frac{-dm}{dt} \left( \frac{1}{a + \Delta} \frac{1}{r_0} \right) = 4\pi Dc_1m_2,$$

where $p_1 = c_1kT$, and $P >> p_1$, $c_1$ is the concentration of vapour at the surface of radius $a + \Delta$. Hence the rate of loss of mass by diffusion is

$$- 4\pi Dc_1m_2 \frac{(a + \Delta)r_0}{(r_0 - a - \Delta)} \text{g. per sec.}$$

But this must be balanced by the rate of arrival of molecules from the surface of the droplet to the region of concentration $c_1$ or

$$4\pi a^2v\alpha(c_0 - c_1) = \frac{4\pi Dc_1(a + \Delta)r_0}{(r_0 - a - \Delta)}.$$

Hence

$$c_1 = \frac{a^2v\alpha c_0}{(a + \Delta)Dr_0 + a^2v\alpha},$$

and

$$\frac{-dm}{dt} = \frac{4\pi aDc_0m_2r_0/(r_0 - a - \Delta)}{(r_0 - a - \Delta)av\alpha + a + \Delta}$$

$$= \frac{4\pi aYc_0m_2}{P\left[ Y/(Pav\alpha) + \left\{ 1 - \frac{(a + \Delta)}{r_0} \left( a + kT/(AP) \right) \right\} \right]}$$

$$= \frac{4\pi aYc_0m_2}{P\left[ Y/(Pav\alpha) + a \left( \frac{AP}{aAP + kT} - \frac{1}{r_0} \right) \right]}.$$  

Since $\Delta = kT/(AP)$. 
Hence

\[-a(da/dt) = \frac{Yc_0m_2}{\rho P\left[\frac{Y}{(Pav\alpha)} + a\left(\frac{AP}{aAP + kT - \frac{1}{r_0}}\right)\right]}\]

or

\[a + H\left[\frac{1}{2}(a + \Delta)^2 - 2\Delta(a + \Delta) + \Delta^2\log(a + \Delta)\right] - Ha^3/3r_0 = -Lt + \text{constant},\]

or

\[a + H\left[\frac{a^2}{2} - a\Delta + \Delta^2\log(a + \Delta)\right] - \frac{Ha^3}{3r_0} = -Lt + \text{constant},\] (11)

where

\[H = \alpha vP/Y = \alpha v/D \quad \text{and} \quad L = \alpha v c_0 m_2/\rho.\]

It should be noted that if the drop evaporates into a region of constant vapour pressure \(c\), then

\[-\frac{dm}{dt} = 4\pi(a + \Delta) Dm_2\left[\frac{c_0a^2v\alpha}{(a + \Delta)D + a^2v\alpha} - c\right].\]

Hence no simple allowance can be made for the influence of the vapour pressure corresponding to concentration \(c\), as can be done for Langmuir’s expression, viz.

\[-\frac{dm}{dt} = 4\pi a Dm_2(c_0 - c).\]

A graphical integration is necessary if the change of radius with time is required for \(c > 0\).

Although equation (11) is the correct form of integration, and should replace the simple equation (9), in much of the work described below the radius of the drop changes only slightly during the run, owing to the sensitive nature of the balance used. Hence equation (10) may be integrated as if the correcting denominator were constant during the run, giving

\[s - s_0 = -\frac{8\pi Y m_2 c_0 t}{\rho P\left[\frac{Y}{(Pav\alpha)} + a\left(\frac{AP}{aAP + kT - \frac{1}{r_0}}\right)\right]}\] (12)

Hence, under the conditions for which \(a\) changes very little during a run, we again have the familiar law, \(s\) a linear function of time, but the proportionality constant varies with pressure in a manner very different from that given by equation (9). The latter gives \(ds/dt\) proportional to \(1/P\), since \(D = Y/P\), i.e. indefinite increase of \(ds/dt\) as \(P\) decreases, whereas equation (12) gives an asymptotic approach of \(ds/dt\) to the vacuum rate. Equation (12) is fully substantiated by the experimental work below. If, however, \(a\) varies considerably during the run then equation (11) must be applied. With drops such as were used for runs in which the radius changed little during the run only the first two terms are significant, but this would not be the case with small drops of radius 0·01 cm. at low pressures (e.g. 0·3 mm. of mercury), as is shown experimentally later.

One may note that at very low pressures of air, or at vapour pressures comparable with air pressures, the above analysis will not apply, since \(D\) will not be a constant between the droplet surface and the wall, owing to the change of \(D\) with pressure. No simple solution for \(c_1\) can be given. However, one can extrapolate equations
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(11) and (12) to \( p = 0 \) with confidence, since the value of \( ds/dt \) is very insensitive to changes of \( P \) when \( P \) is very low, and the difference between the value of \( ds/dt \) calculated from equation (12) and the true result must be very small.

It is assumed that \( p_0 \) is independent of \( P \), which is not quite true, since \( \frac{dp_0}{dP} = \frac{v_{\text{liquid}}}{v_{\text{vapour}}} \), i.e. \( dp_0 = \) of the order of 1 \% for \( dP = 1 \) atm. for dibutyl phthalate. Another point of interest in this connexion is the formation of adsorption complexes in the gaseous phase, owing to the solvent effect of the atmosphere on the vapour. Owing to the large van der Waals’ attractive force of a molecule such as dibutyl phthalate, it is quite possible that in air a cluster of molecules is formed which may be regarded as air molecules adsorbed on the dibutyl phthalate molecule, so that \( m_2 \) is not strictly constant as the air pressure changes.

Equation (12) may be tested by plotting \( ds/dt \) as a function of \( 1/P \) (\( a \) changes only slightly during the run). For large values of \( P \) the plot is a straight line, corresponding to Langmuir’s case, but as \( P \) decreases the correcting term becomes more and more important. If \( ds/dt = q \) for some value of \( P \), and

\[ \frac{-8\pi Y m_2 c_0 t}{\rho P} = q_0, \]  

(13)

\( q_0 \) is readily calculated from the linear portion of the graph, and

\[ \frac{q_0}{q} = Y \frac{P}{P_{avz}} + a \left( \frac{AP}{aAP + kT} - \frac{1}{r_0} \right) \]  

(14)

\[ = \frac{1}{PW} + \frac{1}{1 + kT/(aAP)} - \frac{a}{r_0}, \]  

(15)

where \( W = a v_{avz}/Y \).

Now \( A \) can be roughly computed from the dimensions of the molecule, and the term \( \frac{1}{1 + kT/(aAP)} \) is thus known. Under the conditions of the experiment the calculation is not very sensitive to changes in \( A \). Then if \( q_0 - \frac{1}{q} \left( 1 + kT/(aAP) \right) \) be plotted as a function of \( 1/P \) a straight line should be obtained, from which \( W \) may be calculated. If the vapour pressure is known, \( Y \) may be calculated from \( ds/dt \) for large values of \( P \), and thence \( A \) may be computed, since \( W = av_{avz}/Y \).

Alternatively, \( Y \) may be calculated from diffusion theory. Unfortunately, the latter is not very exact, unless the complicated approach of Chapman and Enskog is adopted. The equation of Meyer, modified to allow for persistence of velocities, seems to be most suitable for calculation. According to this

\[ D = \frac{2}{3(1 + \alpha_{12})} \frac{kT}{\pi S_{12}} \left[ \frac{2kT}{\pi} \left( \frac{m_1 + m_2}{m_1 m_2} \right) \right], \]  

\[ Y = \frac{2}{3(1 + \alpha_{12})} \frac{kT}{\pi S_{12}} \left[ \frac{2kT}{\pi} \left( \frac{m_1 + m_2}{m_1 m_2} \right) \right], \]  

(17)
where $\alpha_{12}$ allows for the persistence of velocities, and is a small term of approximate value $m_1/(m_1 + m_2)$ under the conditions of the experiment. Maxwell's exact solution for the case of repulsion between molecules with an inverse fifth power law gives the same dependence on $P$, but will not be used since the force constants are unknown and since the Maxwell law is in any case unreal. It may be noted that according to equation (16) $D$ is proportional to $T^4$ at constant $P$, whereas experimentally the index of $T$ is greater than 1.5, for water 1.75.

It is of some interest to consider modifications to the above due to the influence of surface tension on vapour pressure. If $\sigma$ is the surface tension and $p_\infty$ the saturation vapour pressure over a plane surface

$$\log \frac{p_0}{p_\infty} = \frac{2\pi m_2 \sigma}{kT a}$$

or

$$p_0 = p_\infty e^{\frac{2\pi m_2 \sigma}{kT a}}$$

Equation (10) becomes, after putting $p_0 = c_0kT$,

$$-\frac{dm}{dt} = \frac{4\pi a Y p_\infty m_2 e^{\frac{2\pi m_2 \sigma}{kT a}}}{kT P}$$

Hence

$$dn\left[ Y/(Pax) + a \left( \frac{AP}{aAP + kT - r_0} \right) \right] = -\frac{2\pi m_2 \sigma}{kT a} - \frac{Y p_\infty m_2 dt}{kT a}$$

Provided that $p_0/p_\infty - 1$ is $\ll 1$ one can expand the exponential and integrate, giving, if the term in $r_0$ be omitted,

$$a + H\{\frac{1}{2}a^2 - aA + A^2 \log (a + A)\} - \frac{2\pi m_2 \sigma}{kT a} - \frac{-Y p_\infty m_2 dt}{kT a} = \frac{-\alpha v p_\infty m_2 t}{kT a} + \text{constant.}$$

As the surface tension effect does not become appreciable before the radius is very small, the droplet has practically vanished before this pressure condition is violated.

III. EXPERIMENTAL. RATES OF EVAPORATION

In order to obtain great sensitivity a quartz microbalance $A$ (figure 1) of the type described by Whytlaw-Gray was used. To one end of the balance was attached a long quartz fibre, terminating in a hook from which was suspended the quartz rod carrying the drop. The balance was counterpoised with quartz weights; detail of the balance is given inset in figure 1. The movement of the pointer $B$ relative to the reference pointer $C$ could be followed by observation through the plate glass window $D$ by means of a travelling microscope reading to 0.001 mm. The window $D$ was ground to fit the pyrex balance case. Surrounding the drop was a copper gauze
cage of radius 1.2 cm., and charcoal was packed in the annular space between the cage and the vessel \( E \). The balance case was mounted on a massive block of metal, and covered with a metal hood, to prevent temperature fluctuations, and the whole apparatus was placed in a thermostated room at 20°. \( F \) was a sintered glass filter to filter particles from the air, \( G, G \) were \( \text{P}_2\text{O}_5 \) tubes, and \( H \) a manometer which was read to 0.01 mm. Low pressures were read on the McLeod gauge. The balance was cleaned by \( \text{HNO}_3 + \text{HCl} \), the glass apparatus by \( \text{KMnO}_4 + \text{concentrated H}_2\text{SO}_4 \).

The end of the quartz rod carrying the drop was drawn out to a very thin fibre, and drops could be made to adhere to the end of this fibre by first forming them at the end of another fibre, touching the fibre points, and then moving them apart. In this way the fibre was uncontaminated with liquid, except at the end. At first the final counterpoise was effected by means of very small quartz weights, but later it was found easier to adjust the weight of the drop. If a clean quartz fibre be plunged through the drop, at right angles to the fibre carrying the drop, and withdrawn, the weight of the drop is slightly reduced. Conversely, the drop may be made to pick up beads of liquid if a fibre carrying such beads is plunged through the drop. Drops were weighed on a micro-analytical balance weighing to \( 10^{-6} \) g., and the quartz balance was calibrated using drops of dibutyl phthalate of different sizes, the weights of which had been determined on the micro-analytical balance. The deflexion versus microscope reading was linear and 1 mm. of the microscope corresponded to \( 2.85 \times 10^{-5} \) g., i.e. a change of weight of \( 2.85 \times 10^{-8} \) g. could be observed. Apiezon grease previously dehydrated was used throughout the apparatus. All air admitted to the apparatus was dried by \( \text{P}_2\text{O}_5 \).
Runs were first made with benzophenone, but the rate of evaporation was found to be inconveniently fast at low pressures. Dibutyl phthalate evaporated much more slowly, and using the sensitive balance it was possible to complete the series of runs over a pressure range of 10–0.1 mm. in a day. With butyl stearate several days were necessary to complete the readings. A repetition of experiments gave good agreement, and no change was observed if the liquids were previously degassed hot in vacuo. It is believed that in view of the extremely low vapour pressure of these liquids no correction is necessary for surface cooling, especially as the two liquids behaved similarly, although the rate for butyl stearate was some fifteen times less than that for dibutyl phthalate. The general trend of results indicates, also, that surface diffusion over the quartz was negligible (cf. especially table 3).

After the drop has been hung on the quartz balance and the apparatus had been assembled, the whole was pumped down for half an hour to an hour to remove any water vapour which is inevitably introduced when the apparatus is opened to the air. Dry air was then admitted to the required pressure, and after about 30 min. deflexion-time readings taken, and the whole repeated at lower pressures. At low pressures some time elapsed before the charcoal attained approximate adsorption equilibrium with respect to air, and readings could be taken; pressure readings were taken throughout the run, to test the constancy of the pressure. Small percentage variations in pressure occurred, although it was occasionally necessary to pump off air which had been desorbed from the charcoal to maintain the constancy. In this low-pressure region large changes in pressure make small changes in rate of evaporation, and hence the pressure was sufficiently static to give negligible variations in rate due to pressure changes.

**Runs using dibutyl phthalate**

Comparatively large drops were first used, of radii 0.5 mm., and the variation in radius over the whole of a series of runs at different pressures was approximately 5% only. During one run at constant pressure the variation in \( a \) was 1% or less, so that equation (12) may be applied with confidence. All runs of this type gave linear plots of surface versus time at constant pressure, even at low pressures, as is seen from figure 2, for a pressure of 0.246 mm.; it will be seen that the change in \( s \) over the whole run is small and hence the conditions of equation (12) apply. A summary is given in table 2. This constancy of \( ds/dt \) indicates that in all cases a steady state had been attained.

In figure 3 these values of \( ds/dt \) are plotted as a function of \( 1/P \). As will be seen, at first the relation is linear, in accordance with equation (9), i.e. Langmuir's formula, but as \( P \) decreases a marked bending away from the initial line occurs. When

\[
q_0/t = \frac{1}{1 + kT/(aAP)}
\]

is plotted against \( 1/P \) a good straight line is obtained (figure 4), in accordance with equation (15), whence the constants of the curve on figure 3 may be calculated. The line goes nearly through the origin, and hence \( a/r_0 \) will be
The rate of evaporation of droplets

Dibutyl phthalate

Figure 2. Air pressure 0.246 mm.

Table 2. Dibutyl phthalate at 20°

<table>
<thead>
<tr>
<th>mean a during run mm.</th>
<th>$P$ mm. of Hg</th>
<th>$-10^5 \times ds/dt = q$ cm.$^2$ per min.</th>
<th>$q_0/q$ cm.$^2$ per min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5150</td>
<td>8.26</td>
<td>0.192</td>
<td>1.001</td>
</tr>
<tr>
<td>0.5210</td>
<td>3.68</td>
<td>0.409</td>
<td>1.053</td>
</tr>
<tr>
<td>0.5117</td>
<td>3.11</td>
<td>0.419</td>
<td>1.214</td>
</tr>
<tr>
<td>0.5155</td>
<td>1.035</td>
<td>1.115</td>
<td>1.372</td>
</tr>
<tr>
<td>0.5081</td>
<td>0.823</td>
<td>1.317</td>
<td>1.460</td>
</tr>
<tr>
<td>0.4992</td>
<td>0.306</td>
<td>2.319</td>
<td>2.230</td>
</tr>
<tr>
<td>0.5052</td>
<td>0.246</td>
<td>2.435</td>
<td>2.642</td>
</tr>
<tr>
<td>0.4850</td>
<td>0.162</td>
<td>2.944</td>
<td>3.320</td>
</tr>
<tr>
<td>0.4732</td>
<td>0.135</td>
<td>2.899</td>
<td>4.044</td>
</tr>
<tr>
<td>0.4951</td>
<td>0.103</td>
<td>2.988</td>
<td>5.142</td>
</tr>
</tbody>
</table>

neglected in equation (15). From the dimensions of the molecule and of a mean 'air molecule' the collision radius was taken as 6.28 Å. The curved line in figure 3 is calculated from these constants, the equation to the line being

$$-10^5 \times ds/dt = \frac{1.583}{P} \left[ \frac{0.43}{P + 1 + 2.444 \times 10^{-3}/(aP)} \right]$$

where $P$ is in mm. of Hg, $s$ in cm.$^2$, $t$ in min. The points are experimental and lie very near the line. Thus equation (12) is substantiated. The choice of $A$ is somewhat arbitrary, but fortunately equation (12) in this region of pressure range is rather
insensitive to change in $A$. The mean value of $a$ was approximately 0.05 cm., so that equation (22) may be written in the more general form, applicable to any radius,

$$-10^6 \times \frac{ds}{dt} = \frac{1.583}{P} \left[ \frac{2.15 \times 10^{-2}}{aP} + \frac{1}{1 + 2.444 \times 10^{-3}/(aP)} \right]$$

(23)

where $P$ is in mm. of Hg, $s$ in cm.$^2$, $a$ in cm., and $t$ in min.

---

**Figure 3**

Dibutyl phthalate

---

**Figure 4**

Dibutyl phthalate
The values of \( q_0/q \) show the magnitude of the departures from Langmuir's theory. Thus at 0·103 mm. pressure the rate of evaporation is approximately one-fifth of that demanded by Langmuir's theory.

Equation (23) may be used to test the theory of a run in which the radius changes appreciably, when \( ds/dt \) should not be constant, but should vary throughout the run. This was found to be true, results for a typical run on a small drop which is allowed to evaporate almost completely being given in table 3. The pressure was 0·309 mm.

| Table 3 |
|------------------|------------------|------------------|------------------|
| \( 10^5 \times \text{wt. of drop} \) | \( \text{time in min.} \) | \( \text{radius in mm.} \) | \( 10^3 \times (\text{radius})^2 \text{ mm.}^2 \) | \( 10^6 \phi(a) \) (equation (24)) |
| \( 584·2 \) | 0 | 0·2370 | 5·617 | 1·527 |
| \( 531·7 \) | 17 | 0·2295 | 5·266 | 1·462 |
| \( 480·1 \) | 34 | 0·2220 | 4·928 | 1·396 |
| \( 417·7 \) | 55 | 0·2119 | 4·491 | 1·311 |
| \( 355·3 \) | 77 | 0·2008 | 4·033 | 1·216 |
| \( 302·8 \) | 97 | 0·1903 | 3·623 | 1·132 |
| \( 241·0 \) | 125 | 0·1764 | 3·112 | 1·016 |
| \( 167·2 \) | 166 | 0·1562 | 2·440 | 0·856 |
| \( 135·8 \) | 184 | 0·1457 | 2·123 | 0·768 |
| \( 106·0 \) | 207 | 0·1342 | 1·801 | 0·677 |
| \( 74·9 \) | 234 | 0·1195 | 1·427 | 0·571 |
| \( 42·2 \) | 271 | 0·0987 | 0·974 | 0·406 |
| \( 24·8 \) | 299 | 0·0826 | 0·682 | 0·286 |
| \( 16·1 \) | 315 | 0·0716 | 0·513 | 0·205 |

Figure 5 shows the lack of constancy in \( ds/dt = 4\pi d(a^2)/dt \); as is seen from figure 6 \( da/dt \) is more constant, but deviates at low values of \( a \). In figure 7 is plotted the Dibutyl phthalate.
Dibutyl phthalate

![Figure 6](image)

Dibutyl phthalate

![Figure 7](image)
The rate of evaporation of droplets

integrated expression from equation (11), expressed in the form, using the constants from equation (23),

\[ 6.167 \times 10^{-2}a + 0.5a^2 + 1.436 \times 10^{-4} \log_{10} (a + 7.895 \times 10^{-3}) = \phi(a) \]

\[ = \text{const.} t + \text{const.} \quad (24) \]

It will be seen that \( d\phi(a)/dt \) is indeed a constant.

In one respect there is a discrepancy between the data of tables 2 and 3. From equation (23) it may be calculated that \( d\phi(a)/dt = -2.038 \times 10^{-6} \), \( t \) being measured in minutes, whereas the slope of the line in figure 7 gives \( d\phi(a)/dt = -4.13 \times 10^{-6} \). Likewise there is a discrepancy of the same order when the slope \( d(a^2)/dt \) in the first part of the curve in figure 5, for small times, when \( a \) is approximately constant, is compared with the calculated value. The experimental rates are greater than those calculated from equation (23) by a factor of approximately 2. It is believed that this is due to the conditions of the experiment, for the larger drops are situated more at the end of the fibre, owing to their greater weight. A drop smaller in weight by a factor of 10 is more pear-shaped owing to the finite thickness of the fibre, and the neck represents a considerable proportion of the total surface. Since the sphere has the smallest surface for a given volume, it follows that the transfer of the data from drops of mass \( 6 \times 10^{-4} \) to \( 6 \times 10^{-5} \) g. will be subject to an error of a geometrical nature, and the smaller drop will evaporate faster than the theory allows. It is probable that the geometrical factor remains approximately constant during a run, once the quartz fibre has been wet to a certain length, so that the function \( \phi(a) \) is indeed linear with time. The time required to evaporate completely an isolated drop free from all attachment is best calculated from experiments on hanging drops over a small range of change in radius.

**Runs on butyl stearate**

In table 4 are summarized the results with butyl stearate, using drops which remained approximately constant in radius during the run. In figure 8, \(-10^6 ds/dt\) is plotted against \(1/P\), and in figure 9, \(g_0/q - \frac{1}{1 + k t/(A a P)}\) is plotted against \(1/P\), taking the collision radius, i.e. the sum of the effective radii of butyl stearate and 

**Table 4. Butyl stearate at 20°**

<table>
<thead>
<tr>
<th>mean (a) during run mm.</th>
<th>(P) mm. of Hg</th>
<th>(-10^6 \times ds/dt) cm.² per min. observed</th>
<th>(g_0/q)</th>
<th>(-10^6 \times ds/dt) cm.² per min. calc. from equation (25)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.542</td>
<td>11.19</td>
<td>0.084</td>
<td>1</td>
<td>0.0848</td>
</tr>
<tr>
<td>0.544</td>
<td>4.77</td>
<td>0.190</td>
<td>1.034</td>
<td>0.192</td>
</tr>
<tr>
<td>0.543</td>
<td>2.33</td>
<td>0.345</td>
<td>1.167</td>
<td>0.366</td>
</tr>
<tr>
<td>0.545</td>
<td>0.743</td>
<td>0.977</td>
<td>2.292</td>
<td>0.959</td>
</tr>
<tr>
<td>0.533</td>
<td>0.309</td>
<td>1.489</td>
<td>2.038</td>
<td>1.467</td>
</tr>
<tr>
<td>0.536</td>
<td>0.238</td>
<td>1.732</td>
<td>2.440</td>
<td>1.647</td>
</tr>
<tr>
<td>0.553</td>
<td>0.164</td>
<td>1.833</td>
<td>3.121</td>
<td>1.875</td>
</tr>
</tbody>
</table>

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Figure 8

Butyl stearate

Figure 9

Butyl stearate
air molecules, as 17 Å; linear plots of \( s \) versus time were obtained for all runs. The line in figure 8 has been calculated from the equation

\[
-10^6 \times \frac{ds}{dt} = \frac{0.980}{P} \left[ \frac{1}{1.957 \times 10^{-2}} \frac{1}{aP} \right. \\
\left. + \frac{1}{1 + 3.337 \times 10^{-4}/(aP)} \right]
\]

(25)

where \( P \) is measured in mm. of mercury, \( a \) in cm., \( t \) in min., and \( s \) in cm.\(^2\); the mean value of \( a \) was 0.542 mm.

IV. EXPERIMENTAL

The determination of the vapour pressure of dibutyl phalate and butyl stearate

The method was a differential modification of that due to Knudsen (1909). The ends of two glass tubes \( A \) and \( B \) were closed by sheet platinum caps fused to the glass (figure 10) and pierced by two circular holes 1.88 and 1.025 mm. in diameter. By means of side tubes the glass tubes could be half-filled with liquid and sealed off. \( A \) and \( B \) were made as nearly alike as possible.

\[\text{Figure 10}\]

The tubes \( A \) and \( B \) were fitted into holes in the solid brass rod \( C \), which was mounted inside a ground joint of the glass apparatus. \( D \) was a silvered Dewar flask which was kept full of liquid air. The lower portion of the apparatus was immersed in mercury at constant temperature.

The apparatus was evacuated by means of a mercury vapour diffusion pump, with a liquid air trap between pump and apparatus, for about an hour. Dry air was
admitted and \( A \) and \( B \) were hung from opposite ends of a micro-analytical balance weighing to \( 10^{-6} \) g. The difference in weight between \( A \) and \( B \) was thus determined. \( A \) and \( B \) were replaced in the apparatus which was maintained at a high vacuum for several hours. The difference in weight between \( A \) and \( B \) was again determined. For \( A \)

\[
p_\infty = \frac{W_1}{t} \left( \frac{RT}{M} \right)^{\frac{1}{2}} \frac{1}{A_1} \left[ \sqrt{2\pi} + \frac{L_1}{R_1} \frac{3\sqrt{\pi}}{4\sqrt{2}} \right] \text{ (approx.)},
\]

where \( p_\infty \) is the vapour pressure, \( W_1 \) the weight lost in time \( t \), \( R \) the gas constant, \( M \) the molecular weight, \( A_1 \) the area of the hole and \( R_1 \) its radius, \( L_1 \) the length of the tube through which the vapour passes (i.e. thickness of platinum) (cf. Clausing 1932; Dushmann 1926). The calculation for the small correction due to the tube length is approximate. Hence \( p_\infty = \frac{k_1 W_1}{tA_1} \left( 1 + \frac{x}{R_1} \right) \), where \( k_1 = \left( \frac{2\pi RT}{M} \right)^{\frac{1}{2}} \) and \( x \) is a constant to allow for the tube resistance.

Similarly

\[
p_\infty = \frac{k_1 W_2}{tA_2} \left( 1 + \frac{x}{R_2} \right).
\]

Hence

\[
W_1 - W_2 = \frac{A_1 p_\infty t}{k_1} \left( 1 - \frac{x}{R_1} \right) - \frac{A_2 p_\infty t}{k_1} \left( 1 - \frac{x}{R_2} \right) \text{ approx. (26)}
\]

When \( x = 0 \) we get

\[
W_1 - W_2 = \frac{p_\infty (A_1 - A_2) t}{k_1} \text{ or } p_\infty = \frac{k_1 (W_1 - W_2)}{(A_1 - A_2) t}. \tag{27}
\]

The second approximation gives

\[
p_\infty = \frac{k_1 (W_1 - W_2)}{(A_1 - A_2) t - \left( \frac{A_1}{R_1} - \frac{A_2}{R_2} \right) xt}. \tag{28}
\]

\( (W_1 - W_2) \) was equal to the difference in readings of the analytical balance, and \( A_1 \) and \( A_2 \) could be measured. Using very pure mercury as a calibrating liquid \( x \) could be determined and the \( x \) term was shown to be small, i.e. the conditions above were fulfilled.

Equation (28) may be rewritten

\[
p_\infty = \frac{k_2 (W_1 - W_2)}{(M)^{\frac{1}{2}} t}, \tag{29}
\]

where \( k_2 \) is a constant determined using mercury and which can be used to find the vapour pressure of the organic liquids.

The mean results were, for \( 20^\circ \),

- dibutyl phthalate: \( p_\infty = 3.05 \times 10^{-5} \) mm. of mercury,
- butyl stearate: \( p_\infty = 1.27 \times 10^{-6} \) mm. of mercury.
The rate of evaporation of droplets

V. The calculation of evaporation and diffusion coefficients

Using Langmuir's equation \( \frac{dS}{dt} = \frac{8\pi Dm^2c_0}{\rho} \) it is clear that the diffusion coefficient may be calculated from the runs on droplets in the high-pressure range if \( c_0 \) be replaced by \( p_0/kT \), its value assuming the vapour to obey the perfect gas laws.

Hence

\[
D \text{ at pressure } P = \left( -\frac{dS}{dt} \right)_{\text{press. }} \frac{\rho kT}{8\pi p_0 m^2} \tag{30}
\]

The diffusion coefficient at atmospheric pressure may be calculated by simple proportion, since \( D \) is inversely proportional to \( P \). The results of § III give, for 20° (putting \( p_\infty = p_0 \)),

- dibutyl phthalate: diffusion coefficient at 760 mm. = 0.031 \( (\rho = 1.048) \),
- butyl stearate: diffusion coefficient at 760 mm. = 0.030 \( (\rho = 0.867) \).

This method of calculating diffusion coefficients from the Langmuir region of evaporation has been previously used in this Department by Mrs Childe (née Stevenson) for more volatile materials than those used in this work; a quartz spiral spring was used (unpublished Ph.D. thesis). Vapour pressures were determined by Knudsen's method. The differential method for vapour pressures, using two evaporating vessels, is new to this work.

The evaporation coefficient may be calculated using equation (12). The first term of the denominator within the brackets is \( Y/Pavz \), and its numerical value is known from equations (23) and (25), e.g. equation (23) gives \( \frac{Y}{Pavz} = 2.15 \times 10^{-2} \). Hence for dibutyl phthalate \( z = Y/(2.15 \times 10^{-2}P) \). Since \( Y = DP \) and \( D \) has already been determined for any value of \( P \), \( Y \) may be calculated; for dibutyl phthalate \( Y \) is clearly 0.031 x 760 in the units of pressure used, mm. of Hg. Hence \( z \) can be calculated. The results for the evaporation coefficient of dibutyl phthalate and butyl stearate at 20° are respectively 0.28 and 0.35.

VI. Conclusion and discussion

The work reported above on the evaporation of droplets at various air pressures leaves no doubt that Fuchs's equation represents the facts, and it is to be expected that the application of this equation to conditions other than those investigated, e.g. to conditions of very small radius and atmospheric pressure, will give an equally true picture of the evaporation behaviour of droplets.

Some biological and industrial applications are of interest. Thus evaporation from the pores of the skin of animals, or the stomata of plants will be enhanced by the smallness of these openings, for a given total area of evaporating water surface,
provided that no interference due to vapour occurs between neighbouring openings. For evaporation from hemispherical caps of radius $a$ it is seen that

$$
\text{rate of evaporation per unit area} = \frac{Dc_0 m_2}{\nu \alpha + a + \Delta}.
$$

When $a$ is large, rate of evaporation per unit area is

$$
\frac{Dc_0 m_2}{a_1}.
$$

Hence

$$
\left(\frac{\text{rate of evaporation per unit area for small drops}}{\text{rate of evaporation per unit area for large drops}}\right) = \frac{a_1}{D \nu \alpha + a + \Delta}, \quad (31)
$$

where $a_1 \gg a$. For water at atmospheric pressure of air $D/(\nu \alpha) = 0.001$ approx., taking $\alpha = 0.01$, $D = 0.2$ approx. Hence the ratio in equation (31) becomes

$$
\frac{a_1}{0.001 + a} \approx ,
$$

which with $a_1 = 1$ cm. and $a = 10^{-4}$ cm. gives an increase by a factor of approx. 900; with $a_1 = 1$ cm. and $a = 10^{-3}$ cm. the factor is approx. 500. It should be noted that in this calculation no modification of the theory is introduced to allow for the presence of a liquid edge. Moreover, in practice these factors will be cut down by vapour interference between evaporating surfaces. Other applications are in the drying of foodstuffs by spraying, where there will be a large factor increasing the rate of evaporation even when the extra surface is allowed for, and the possibility of separating constituents of oils by evaporation from sprays.

We wish to express our thanks to the Ministry of Supply for permission to publish this work.

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