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Solution of ordinary and partial differential equations

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The escape of molecules from a plane surface into a still atmosphere

BY K. J. BROOKFIELD, H. D. N. FITZPATRICK, J. F. JACKSON, J. B. MATTHEWS AND E. A. MOELVYN-HUGHES

(Communicated by A. R. Todd, F.R.S.—Received 29 October 1945—Revised 23 January 1946)

When molecules escape from solids or liquids into a gaseous atmosphere, they do so at a rate which is governed by certain inherent properties of the condensed systems and by the relative values of the saturation pressure of the condensate and the total pressure of the atmosphere. Present considerations are restricted to systems wherein the saturation pressure is a small fraction of the ambient pressure, and to liquids evaporating from plane surfaces. A theory is advanced which embraces the diffusion conditions formulated by Maxwell (1890) and the vacuum conditions investigated by Knudsen (1915), and is cast in such a form as to make accessible to experiment the determination of the coefficients of diffusion and accommodation by novel means.

The escape of molecules from the surface of a liquid or solid into a gaseous atmosphere resembles in many respects the dissolution of a solid into a liquid. The hypotheses of dissolution advanced by Noyes & Whitney (1897) and by Nernst (1904) have been synthesized into a general theory by Berthoud (1922). A method
closely resembling that of Berthoud has later and independently been applied by Fuchs (1934) to the problem of vaporization from spherical surfaces. Following these workers, the mechanism of the escape of molecules from a plane liquid surface may be formulated as follows.

The number of molecules of liquid escaping per second from a plane surface of area $S$ is

$$\frac{dN}{dt} = S n_s \bar{v} - S n \bar{u} \alpha,$$

(1)

when $N$ = the total number of liquid molecules in the system,

$n_s$ = the number of liquid molecules per unit area of surface,

$\bar{v}$ = the average probability per second that a liquid molecule evaporates,

$n$ = the number of molecules per unit volume of vapour,

$\bar{u} = (kT/2\pi m)^{1/2}$, where $T$ is the absolute temperature, and $m$ is the mass of a single molecule,

and $\alpha$ = the accommodation coefficient.

At the equilibrium state, $-dN/dt = 0$ and $n = n^0$, the saturation concentration of vapour; hence

$$n_s \bar{v} = n^0 \bar{u} \alpha.$$

(2)

Eliminating $n_s \bar{v}$ from equations (1) and (2), then

$$\frac{dN}{dt} = S \bar{u} \alpha (n^0 - n).$$

(3)

Near the surface, a stationary concentration of vapour molecules is rapidly established due to the balancing of the natural escaping tendency of liquid molecules on the one hand, and the hindrance to escape offered by surrounding gas or vapour molecules on the other hand. The stationary concentration, $n'$, of vapour molecules thus established is less than $n^0$, and, in the stationary state, the rate of vaporization consequently becomes

$$\frac{dN}{dt} = S \bar{u} \alpha (n^0 - n').$$

(4)

The rate of loss of molecules due to diffusion, is, by Fick’s law,

$$\frac{dN}{dt} = -SD \left( \frac{\partial n}{\partial x} \right),$$

(5)

where $D$ is the coefficient of diffusion, and $\partial n/\partial x$ is the concentration gradient. Application of the general diffusion law

$$\frac{dn}{dt} = D \frac{d^2 n}{dx^2},$$

(6)

to the stationary state gives the relation

$$\frac{dn}{dt} = 0.$$

(7)
Escape of molecules from a plane surface into a still atmosphere

The molecular concentration, \( n \), at a fixed distance, \( x \), from the surface, is thus independent of time. As \( D \) itself cannot be zero, it follows that

\[
\frac{d^2n}{dx^2} = 0.
\]  

(8)

On integrating, one obtains, for the dependence of the stationary concentration on the distance, \( x \), from the surface, the relation

\[
n = ax + b.
\]  

(9)

The constants, \( a \) and \( b \), are determined by the boundary conditions

\[
n = n', \quad x = \Delta, \]  

(10)

and

\[
n = 0, \quad x = H, \]  

(11)

so that

\[
n = n' \frac{H - x}{H - \Delta},
\]  

(12)

and consequently

\[
\frac{\partial n}{\partial x} = \frac{n'}{H - \Delta},
\]  

(13)

so that

\[
\frac{dN}{dt} = SD \frac{n'}{H - \Delta}.
\]  

(14)

Combining equations (4) and (14), then

\[
n' = n^0 \frac{\bar{u}z(H - \Delta)}{\bar{u}z(H - \Delta) + D}.
\]  

(15)

Eliminating \( n' \) from equation (15) and either equation (4) or equation (14), the expression

\[
-\frac{dN}{dt} = SDn^0[(H - \Delta) + (D/\bar{u}z)]^{-1}
\]  

(16)

is obtained, which reduces, when \((H - \Delta)\) is small, to

\[
-\frac{dN}{dt} = \bar{u}zn^0,
\]  

(17)

as in the theory of Knudsen (1915), and when \((H - \Delta)\) is relatively large \((> 10^{-4} \text{ cm.})\) to

\[
-\frac{dN}{dt} = SD \frac{n^0}{H - \Delta},
\]  

(18)

as in the theory of Maxwell (1890). The thickness, \( \Delta \), of the diffusion layer must not, of course, be confused with Maxwell’s correction factor of \((2/5)d\), which must be added to the height, \( H \), of an open cylinder when it is comparable with the diameter, \( d \).

If \( w \) is the weight of liquid vaporizing per second from an area, \( S \), then

\[
w = -m \frac{dN}{dt},
\]  

(19)
and therefore the general expression for the rate of loss of weight becomes

\[ w = mSDn^0[(H - \Delta) + D/\bar{u}x]^{-1}, \]  

which may conveniently be rewritten as follows:

\[ \frac{S}{w} = \frac{(D/\bar{u}x) - \Delta}{mn^0D} + \frac{H}{mn^0D}. \]  

The measurable quantities \( S/w \) and \( H \) are thus linearly related, and the gradient of the curve should have the constant value of \( 1/mn^0D \), from which the diffusion coefficient, \( D \), can be obtained, provided the saturation concentration, \( n^0 \), is known. Then, in fact,

\[ D = \left( \frac{mn^0}{d(S/w)/dH} \right)^{-1}. \]

The positive intercept made by the curve on the \( (S/w) \) axis, corresponding to \( H = 0 \), should, in principle, allow of an evaluation of the accommodation coefficient, \( \alpha \). In practice, however, it is difficult to measure the height \( H \) absolutely, because of the ill-defined nature of the boundary corresponding to \( n = 0 \). The method, therefore, while yielding reliable values for the diffusion coefficient, \( D \), can yield only approximate values for the accommodation coefficient \( \alpha \).

**APPARATUS AND PROCEDURE**

A straight-sided glass weighing bottle, \( A \), of cross-sectional area \( S \), is placed inside a wider tube \( C \), with a little mercury in the bottom to ensure thermal contact (see figure 1). A tube \( B \), which slides easily into \( A \), is closed at the bottom with copper gauze, and contains granular, dust-free, freshly degassed charcoal. A known weight of liquid is placed in \( A \), and \( B \) is slid down till the gauze is at a height \( H \) above the liquid surface, being then arrested by a rim of sealing wax \( DD \). The apparatus

![Figure 1. Glass apparatus for measuring diffusion coefficients.](image)
is immersed in a thermostat at a temperature which is maintained constant to within $\pm 0.05^\circ\mathrm{C}$. The weighing bottle is weighed and placed in the outer tube. The charcoal tube $B$ is then lowered carefully into position and the time noted. After a suitable interval of time the procedure is reversed, the time again being noted, and the loss of weight of the weighing bottle obtained. $w$, the loss of weight per second, is thus found. When $S/w$ is plotted against $H$, a straight line results, in agreement with equation (21). The gradient of the line, obtained by the method of least squares, is equated to $(mn^0D)^{-1}$. Values of $n^0$ are obtained from the vapour pressure $p^0$ by assuming the ideal gas laws to hold:

$$n^0 = p^0/kT.$$  \hspace{1cm} (23)

The adopted total pressure is the mean value holding for the period of the runs, and is obtained from the laboratory barometer chart. The height $H$ is determined by cathetometer readings, combined with a knowledge of the density and total amount of liquid employed. The uniform area, $S$, of the liquid surface is deduced by observing the increase in height occasioned by introducing a known weight of mercury into the vessel.

At temperatures above $40^\circ\mathrm{C}$, the glass apparatus is found to be not so satisfactory because of the softening of the sealing wax, so an improved apparatus was constructed (figure 2). The principle remains the same, but the glass tube containing the charcoal is replaced by a mild steel tube. The tube is held in position by means of an adjustable collar, which in one design rested on the top of the glass vessel, and in another on the outer tube (see figure 2). The outer tube is also made of mild steel, and screwed into a heavy base, the joint being made watertight by a rubber washer. The height of the charcoal above the liquid is measured by adjusting the collar to one of a series of marks that had been etched on the inner tube, the height from the bottom of the tube having previously been measured with a cathetometer. The depth of liquid in the tube is calculated from its weight and density and the area of the glass vessel, and is subtracted from the height corresponding to the position of the etched mark.

**Figure 2.** Improved mild steel apparatus for measuring diffusion coefficients.
K. J. Brookfield and others

Results

The linear relationship required by equation (21) between \((S/w)\) and \(H\) has been established for a number of liquids over a fairly wide range of diffusion conditions. The data given in table 1 have been obtained for two liquids which are typical of a large number examined.

| vapour          | \(p^0\)   | \(n^0\)     | \(d(S/w)/dH\) | \(D(\text{cm}^2/\text{sec.})\)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>furfural</td>
<td>25-0</td>
<td>2-03</td>
<td>6-61 \times 10^{16}</td>
<td>1-085 \times 10^7</td>
</tr>
<tr>
<td></td>
<td>50-0</td>
<td>9-55</td>
<td>28-8 \times 10^{16}</td>
<td>0-207 \times 10^7</td>
</tr>
<tr>
<td>methyl salicylate</td>
<td>25-0</td>
<td>0-108</td>
<td>3-515 \times 10^{15}</td>
<td>1-392 \times 10^7</td>
</tr>
<tr>
<td></td>
<td>50-0</td>
<td>0-717</td>
<td>21-6 \times 10^{15}</td>
<td>1-304 \times 10^6</td>
</tr>
</tbody>
</table>

The results are not extensive enough to allow a decision as to the exact form of the temperature dependence of the diffusion coefficient, which, according to the theory of activated diffusion, takes the form

\[ D = A T^{3/2} e^{-B/RT}. \]

\(B\), which is known to be small, is therefore assumed to be zero, and the values of \(A\) given in table 2 are obtained.

| substance    | \(A\)                  | \(\sigma_{12} \times 10^8 \text{(cm.)}\)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>furfural</td>
<td>((1-77 \pm 0-08) \times 10^5)</td>
<td>4-54</td>
</tr>
<tr>
<td>methyl salicylate</td>
<td>((2-01 \pm 0-43) \times 10^5)</td>
<td>4-61</td>
</tr>
</tbody>
</table>

According to the Stefan–Maxwell theory, the constant \(A\) is given in terms of the sum, \(\sigma_{12}\), of the molecular radii of the molecule diffusing and the molecules through which it diffuses:

\[ A = \frac{2k}{3\pi P \sigma_{12}^3} \left(\frac{2k}{\pi m} \left(1 + \frac{m}{m_i}\right)\right)^{1/2}. \]

Here, \(k\) is Boltzmann’s constant, \(m\) is the mass of one molecule of liquid, \(m_i\) the mass of a ‘molecule’ of air, and \(P\) the total pressure of one atmosphere. The values of \(\sigma_{12}\) derived for furfural and methyl salicylate are given in table 2.

Experimental determination of the coefficient of diffusion of water vapour in air

As a check upon the method, the diffusion of water vapour into still air at atmospheric pressure and at various temperatures has been measured. Because the diffusing molecules are now lighter than air ‘molecules’, the apparatus has to be so modified that diffusion takes place downwards. Sulphuric acid replaces charcoal as the absorbing medium. A large, wide-necked bottle, containing water to the
depth of a few centimetres, was placed in a thermostat up to the neck (figure 3). The air inside the bottle was assumed to be always saturated. A straight-sided weighing bottle, with area \( S \), containing concentrated sulphuric acid, the surface of which was at a distance \( H \) below the rim, was placed inside the large bottle on a rubber bung which projected above the water surface as an island. The dimensions of the large bottle greatly exceeded those of the weighing bottle. It was assumed that the concentration of the water vapour was the saturation value at the top of the weighing bottle, and zero at the surface of the sulphuric acid. The weighing bottle was weighed, the stopper removed, and placed in the large bottle. After a time \( t \), the weighing bottle was removed, restoppered and weighed again, the gain in weight being noted. The ratio \( S/w \), where \( w \) is the rate of gain in weight, was plotted against \( H \), and the slope of the straight line found. The vapour densities were calculated from the vapour pressures given in Landolt-Börnstein's Tabellen (table 3).

![Figure 3. Apparatus for measuring diffusion coefficient of water vapour into air.](image)

**Table 3. Vapour pressures and vapour densities for water**

<table>
<thead>
<tr>
<th>( T(°K) )</th>
<th>( p^0(\text{mm}) )</th>
<th>( mn^0 \times 10^4(\text{g.}./\text{c.}.) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.1</td>
<td>23.76</td>
<td>2.304</td>
</tr>
<tr>
<td>308.1</td>
<td>42.19</td>
<td>3.957</td>
</tr>
<tr>
<td>318.1</td>
<td>71.90</td>
<td>6.533</td>
</tr>
</tbody>
</table>

The results are summarized in tables 4 and 5. Except at the highest temperature, when the partial vapour pressure is a significant fraction of the total pressure, \( D \) is roughly proportional to \( T^4 \). The average value of \( D/T^4 \) may be taken as \( 4.82 \times 10^{-5} \).

From the Stefan-Maxwell equation

\[
D = \frac{2}{3\pi(n + n_i) \sigma_{12}^2 \left( \frac{2kT}{\pi m} \left( 1 + \frac{m_i}{m} \right) \right)^\frac{1}{2}},
\]

(26)
the mean molecular diameter of the water and air 'molecules' is thus found to be \(3.61 \times 10^{-8}\) cm. This value lies between that of 4.14 A found from transport phenomena, and 2.99 A from the constants 'b' of van der Waals's equation.

The data of Winkelmann (1884) and of Trautz & Müller (1935), as summarized by Dorsey (1932), give the figures in table 6 as the most dependable values hitherto obtained for the coefficients of diffusion of water in air.

**Table 4. Diffusion of water vapour into air**

\[ S = 4.5 \text{ cm}^2 \]

<table>
<thead>
<tr>
<th>( ^\circ \text{K} )</th>
<th>( P ) (mm.)</th>
<th>( H ) (cm.)</th>
<th>( t ) (sec.)</th>
<th>( w ) g. g/sec.</th>
<th>( S/w ) cm暴 g/sec.</th>
<th>( d(S/w)/dH ) cm暴 g/sec.</th>
<th>( D ) cm暴 sec.暴</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.1</td>
<td>750</td>
<td>2.1</td>
<td>7200</td>
<td>0.069</td>
<td>9.6 \times 10^{-6}</td>
<td>4.70 \times 10^{5}</td>
<td>1.74 \times 10^{5}</td>
</tr>
<tr>
<td>308.1</td>
<td>752.5</td>
<td>1.6</td>
<td>2700</td>
<td>0.058</td>
<td>2.15 \times 10^{-5}</td>
<td>2.11 \times 10^{5}</td>
<td>9.54 \times 10^{4}</td>
</tr>
<tr>
<td>318.1</td>
<td>754</td>
<td>1.6</td>
<td>1800</td>
<td>0.068</td>
<td>3.78 \times 10^{-5}</td>
<td>1.10 \times 10^{5}</td>
<td>5.37 \times 10^{4}</td>
</tr>
</tbody>
</table>

**Table 5. Coefficient of diffusion of water vapour in air at 1 atm.**

<table>
<thead>
<tr>
<th>( ^\circ \text{K} )</th>
<th>( D ) (cm暴 g/sec暴)</th>
<th>( (D/T^2) \times 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.1</td>
<td>0.247</td>
<td>4.80</td>
</tr>
<tr>
<td>308.1</td>
<td>0.262</td>
<td>4.84</td>
</tr>
<tr>
<td>318.1</td>
<td>0.283</td>
<td>5.00</td>
</tr>
</tbody>
</table>

**Table 6. Comparison with previous work on water**

<table>
<thead>
<tr>
<th>( ^\circ \text{C} )</th>
<th>( D ) (Dorsey)</th>
<th>( D ) (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.257</td>
<td>0.247 ± 0.005</td>
</tr>
<tr>
<td>35</td>
<td>0.271</td>
<td>0.262 ± 0.005</td>
</tr>
<tr>
<td>45</td>
<td>0.286</td>
<td>0.283 ± 0.005</td>
</tr>
</tbody>
</table>

The method outlined in this work thus provides reliable values of the coefficient of diffusion, and may yet be developed to yield equally reliable values of the coefficient of accommodation.

We are indebted to Professor D. Brunt, of the Imperial College of Science and Technology, for valuable criticism of this work, and to the Chief Scientific Officer of the Ministry of Supply for permission to publish it.
On the propagation of electromagnetic waves through the atmosphere

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A general method of tackling the problem of the propagation of electromagnetic waves in the ionosphere has been developed and the current methods of Appleton, Hartree, Saha, Rai and Mathur, etc., have been deduced as special cases from the general results. The different assumptions by Appleton, Hartree, Bose, Booker and Rai, as regards the condition of reflection of the waves from the ionosphere, have been shown to be identical. A symbol-correspondence chart for the different symbols used by the different workers has been given to facilitate the understanding of the parallelism between the different methods. Polarization of the radio waves have been discussed fully.

INTRODUCTION

The existence of the region of the atmosphere which we now call ‘ionosphere’ was first postulated by Balfour Stewart (1878) to explain the daily variation of the earth’s magnetic field, but it was in 1902 that Kennelly and Heaviside pointed out that the hypothesis of a conducting layer at a height of about 100 km. can explain the paradoxical result that wireless signals can, in spite of the curvature of the earth, be propagated over great distances. It was, however, as late as 1925, when its existence was first directly proved by Appleton & Barnett (1925) in England by the slow variation of the transmitter wave-length and, later, by Breit & Tuve (1926) in the U.S.A. by the use of the pulse technique method. The latter method, which is now in universal use for investigation of the ionosphere, gives apparently spectacular exhibition of its existence, from the appearance of the reflected echo on the cathode ray oscillograph on a properly calibrated time axis.

The detailed interpretation of these echoes, however, is not so simple, as has been emphasized by various workers, and the reason is twofold: (a) experimental, and (b) theoretical.