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XXXIX. *Thermal Transpiration and Radiometer Motion.*
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PART I.—*Thermal Transpiration.*

THE comparative neglect into which the radiometer has fallen is probably the natural compensation for the exalted interest of its two or three years' reign over the scientific imagination twenty years ago. In reading amongst the papers about it published at that time, one gets an impression of the laboratory of Crookes as of an arsenal where night and day the equipment of a great expedition into the unknown was being pushed on under the sleepless eye of a patriot leader; but in the answering bustle outside, Stokes, Schuster, Stoney, Fitzgerald, Pringsheim, Reynolds, and others soon showed that the new conquest was simply an outlying part of the Kinetic Theory of Gases. Or, to vary the figure, Crookes appears as a friendly counsel subjecting Nature to a passionate and eloquent cross-examination with his fellow physicists as judge and jury bringing in a verdict for Kinetic Theory. And then the interest died away rapidly, perhaps mostly on account of Reynolds's great paper "On certain Dimensional Properties of Matter in the Gaseous State" (Phil. Trans. clxx.), which was probably held to settle the essential points of general interest in radiometer motion as consequences of the kinetic theory of gases, especially as the same train of reasoning had led him to his discovery of

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Thermal Transpiration with the beautiful experimental establishment of its simple quantitative laws, simple in the illumination of his theory, but complex enough without it. Unfortunately the mathematical form of Reynolds's theory is wearily cumbersome; one gathers that Maxwell found it distasteful, and Fitzgerald (*Phil. Mag.* [5] xi.) describes it as inelegant and unnecessarily elaborate.

A great objection to Reynolds's mathematics is that it does not join on naturally with that developed for the general purposes of the kinetic theory of gases; it has a certain interest of individuality about it, but this fails to compensate for the waste of mental energy to the reader who has to adapt himself to it. But what appears to me to be the fatal objection to Reynolds's mathematical method, is that it takes the mind away from definite physical concepts of the actual operation of the causes of thermal transpiration and radiometer motion; and the object of the present paper is to construct a theory of these that will fall into line with the current kinetic theory of gases and keep the physics of the phenomena to the fore.

The most convenient starting-point is the laws discovered by Clausius (*Pogg. Ann.* cxv. 1862) for the conduction of heat in gases. In a vertical cylinder of gas, bounded by a solid wall impermeable to heat and two conducting plane ends, the lower at temperature θ_1 and the upper at a higher temperature θ_2 , when the flow of heat has become steady, the pressure throughout the cylinder is constant, and the temperature θ at distance x from the lower end of the cylinder whose whole length is l is given by the equation

$$\theta^{\frac{3}{2}} = \theta_1^{\frac{3}{2}} + (\theta_2^{\frac{3}{2}} - \theta_1^{\frac{3}{2}})x/l,$$

and the distribution of density is determined in accordance with these two results. Now in the establishment of the law of the temperature, it was shown by Clausius that in a mass of gas which is not uniform in temperature there is motion of the gas in the direction of variability; but it is assumed (as it can easily be proved) that under ordinary circumstances this motion can never produce an appreciable departure from uniformity of pressure, because the rate at which a variation of pressure throughout a mass of gas is effaced is so rapid in comparison with the motion which might produce a variation of pressure, that such a variation can never get itself established to an appreciable extent. But when in place of an ordinary cylinder we consider a very fine tube, we must take account of the effect of viscosity in reducing the velocity with which an inequality of pressure along the tube can get itself effaced; and if the tube becomes fine enough, this velocity

may be reduced till it is merely comparable with, or even much smaller than, the velocity with which motion caused by varying temperature may be tending to establish inequality of pressure. Thus, then, in discussing the conductivity of gas in a nonconducting tube of capillary dimensions, we could no longer enjoy the convenient simplification which comes into the problem of Clausius when he writes the pressure constant as one of his fundamental equations, but from purely kinetic considerations we should have to determine the laws both of the variation of pressure and of temperature associated with the steady flow of heat. But in the actual problem of thermal transpiration if we lose one simplification we gain another, because we have to do, not with nonconducting walls, but with walls conducting so well and with so large a thermal capacity compared to that of the gas, that the law of variation of temperature is fixed entirely by the properties of the solid; so that the gas, if subject to varying pressure, is also subject to a fixed law of temperature which we are freed from having to find.

In the kinetic theory the molecules which are considered characteristic of an element are those that have experienced a collision in it; those passing through without collision are taken account of in the elements where they do collide. If the element is a short length of our tube, we do not consider the molecules rebounding from the solid wall as characteristic unless they also encounter other molecules in the element, and thus we might appear to be neglecting the most characteristic molecules of the element. But this is not really so, because those reflected from the side of the tube and moving to a cooler element, as a rule collide with those coming from a still cooler element and including an equal number that have come from its walls, so that the colliding pairs on the average possess the qualities that are to characterize the element in which they collide. Thus, then, if we do not have to take account of reflexion from the walls of the tube, we can consider the gas in it as part of an indefinite mass such that the temperature throughout a plane perpendicular to the axis is the same as that in the section of the tube made by the plane. We wish to find the number of molecules crossing any section of the tube. This is done by Clausius in his theory of conduction in gases, and with greater refinements of accuracy by Tait (*Trans. Roy. Soc. Edinb.* xxxiii.); but for the sake of clearness we will make the calculation here to a degree of accuracy suitable for present requirements.

If there are n molecules per unit of volume in a small element dB , and each has ν encounters per second, then the

number of molecules colliding in a second in dB is $nv dB$. It is not worth while to take account of Maxwell's law of velocities; and all molecules will be supposed to have the average velocity v and travel the mean free path λ between two encounters, so that $\nu = v/\lambda$. But we must take account of the variation of λ with direction; for a molecule travelling from a particular point has a longer path in the direction of diminishing density and a shorter path in that of increasing density, with a maximum parallel to the axis in one direction and a minimum in the other; while the path at right angles to the axis is the mean of the maximum and minimum, and is indeed the mean path λ of all molecules leaving that point. Let λ_m be the maximum value there; then it is equal to the minimum at distance λ_m along the axis of the tube, and must therefore be equal to the mean value at distance $\lambda_m/2$; thus, then, $\lambda_m = \lambda + \lambda_m d\lambda/dx/2$, or $\lambda_m = \lambda + \lambda d\lambda/dx/2 = \lambda(1 + \lambda'/2)$. On the same principle, the free path of a molecule that leaves the point in any direction so that the projection of its path on the axis of the tube is x , has a value $\lambda + x\lambda'/2$. Of the number $nv dB/\lambda$ of molecules that in unit time have a collision in dB , the fraction that cross a plane at any distance is found by drawing from the centre of dB as origin the surface whose polar equation is $\rho = \lambda + x\lambda'/2$, and estimating the solid angle subtended at the origin by the segment of this surface cut off by the plane, supposed to be at distance x , as a fraction of 4π . This is the required fraction, namely $\{1 - x/(\lambda + x\lambda'/2)\}/2$, or $(1 - x/\lambda + x^2\lambda'/2\lambda^2)/2$ nearly.

Thus the number of molecules colliding in dB and crossing the plane before colliding again is in unit time

$$nv dB (1 - x/\lambda - x^2\lambda'/2\lambda^2)/2\lambda,$$

in which we have changed the sign of λ' so as to transfer the origin from dB to the plane. Now dB may be taken as $A dx$ where A is the area of section of the tube; the total number crossing the plane from the tube on one side of it in unit time is the integral from 0 to λ_1 of $Anv(1 - x/\lambda - x^2\lambda'/2\lambda^2)dx/2\lambda$, where λ_1 is the maximum free path at such a distance from the plane that a molecule after colliding there and travelling perpendicular to the plane collides again just at the plane. Now $\lambda = c/n$, where c is a parameter depending only on the size of the molecules; thus the number is

$$\int_0^{\lambda_1} A n^2 v (1 - nx/c - n^2 x^2 \lambda' / 2c^2) dx / 2c . . . \quad (1)$$

Now if n_0 and v_0 are the values of n and v at the plane

we can write $n = n_0 + x \frac{dn}{dx} = n_0 + n'x$ and $v = v_0 + v'x$ and $\lambda_1 = \lambda_0 + \lambda' \lambda_0 / 2$; substituting these values, integrating, neglecting products and squares of $n'v'$ and λ' , and dropping the suffix 0 as of no more use we get

$$Anv\{1/4 + \lambda(v'/v - \lambda'/\lambda)/12\} \quad . \quad . \quad . \quad (2)$$

The number crossing in unit time from the negative side of the tube is obtained from this by changing the sign of n' and v' so that the total gain in unit time from the positive to the negative side of the plane is (since $\lambda'/\lambda = -n'/n$)

$$Anv\lambda\left(\frac{n'}{n} + \frac{v'}{v}\right)/6 \quad . \quad . \quad . \quad . \quad (3)$$

which amounts to the same thing as if the gas had a velocity

$$u = -v\lambda\left(\frac{n'}{n} + \frac{v'}{v}\right)/6 \quad . \quad . \quad . \quad . \quad (4)$$

along the tube; but the result holds not only for a tube, but for any space filled with gas and for any direction in it in which n' and v' are the rates of variation of n and v . The law connecting n and v with position in the general case must be complicated, but for a gas in contact with a solid the thermal capacity of the latter is so great as to make v' and v for the gas at the surface the same as for the solid there, so that the problem simplifies to that of getting the law of n . At a distance z from the solid surface the conditions of n and v are still such as to tend to produce a velocity like u , so that in the general case we have to consider the effect of viscosity in causing these velocities to influence one another. The friction per unit area parallel to the surface at z is $\eta du/dz$, and the state of the gas cannot be steady till this is constant. Returning to the case of a tube, we see that the steady state will be reached when the velocity v and n are constant throughout a section, and the velocity u is therefore also constant throughout the section. Now under ordinary circumstances there would be friction between the gas and the tube over the whole surface, and therefore in this case there must be an action between the solid and the gas equal and opposite to the friction, that is to say, that the solid wall of a tube along which heat is being conducted in constraining the gas to take its temperature and share in the conduction of heat exercises a traction on it. The total friction does not exactly neutralize the total traction, but leaves a small resultant part of it which we can determine thus: suppose the tube connects two infinite spaces at the same temperature

as the ends of the tube, the gas enters at one end with velocity 0 and leaves at the other with velocity u ; in unit time the mass $nmAu$ passes out with momentum $nmAu^2$, and this therefore is the force exerted by the tube on the gas in it; this force acts only near the entrance in the part where the velocity is rising from 0 to u , so that in this part the total traction exceeds the total friction by $nmAu^2$. In the velocity u we have the cause of thermal transpiration, while that of radiometer motion is implied in the equation

$$\text{total unequilibrated traction} = nmAu^2. \quad . \quad . \quad (5)$$

If the spaces at the ends of the tube instead of being infinite are finite, the gas will flow till a fall of pressure is established to arrest it, but we cannot secure that $u=0$ all over any section of the tube by an application of pressure, because the flow established by excess of pressure at one end of a capillary tube is not of uniform velocity throughout each section, but has a maximum velocity at the axis and a minimum at the surface; hence to secure that there shall be no total flow in such a tube we have to establish a difference of pressure which acting alone would discharge a volume Au per unit time in the opposite direction to that of u . Thus, then, our solution for the motion in a conducting tube when there is no total flow of gas along it consists of the superposition of a uniform velocity u and opposite velocities varying in conformity with the laws of flow in a capillary tube of uniform temperature, the result being to give a surface of zero velocity somewhere between the axis and the wall, with a circulation going up between this surface and the wall, and backward between this surface and the axis.

According to the theory of the flow of gas in a capillary tube, if dp/dx or p' is the rate of fall of pressure along the tube, where the pressure is p and η is the viscosity, then B , the volume measured at p delivered in unit time from a circular tube of radius R (O. E. Meyer, Pogg. *Ann.* cxxvii.), is

$$B = \pi p' R^4 / 8\eta \quad . \quad . \quad . \quad . \quad . \quad (6)$$

when the slipping of the gas on the walls can be neglected; but if slipping is to be taken account of let its coefficient be ζ ; then

$$B = \pi p' R^4 (1 + 4\zeta/R) / 8\eta \quad . \quad . \quad . \quad . \quad (7)$$

As the importance of ζ depends entirely on its ratio to R , and as we wish to discuss tubes of any minuteness whatever, a discussion of slipping becomes of first-rate importance to the subject in hand.

Kundt and Warburg (*Pogg. Ann.* clvi.) showed experimentally the existence of slipping by its effect on the apparent coefficient of viscosity at low enough densities of the gas in an oscillating disk apparatus for measuring viscosity, and they adduced theoretical reasons for the necessity of its existence and for some of its properties; they also measured its amount and verified some of its laws, and a little later Warburg demonstrated the slipping of gas on the walls of capillary tubes (*Pogg. Ann.* clix.)

That slipping is a necessary consequence of the kinetic theory can easily be shown. Consider gas between two solid parallel planes, one fixed and the other moving parallel to itself with velocity w ; then in the steady state there is a constant rate of diminution of velocity dw/dx in the gas between the plates. Suppose the molecules of the solid, like those of the gas, to be smooth spheres oscillating, but their centres at the surface having a mean position forming a plane. Consider a molecule of gas in collision with a molecule of solid; if its velocity of rebound makes an angle less than $\pi/2$ with the normal to the plane, the molecule has little chance of colliding with another surface molecule of the solid and is directly reflected; the majority of these directly reflected molecules of gas must strike the molecules of solid near their most prominent points, and therefore acquire from them very little of their velocity parallel to the plane; thus a certain fraction f of the molecules of gas that encounter the surface leave it with practically the same velocity parallel to it as that with which they approached; the remaining fraction $1-f$, or those which at the instant of rebounding from a surface molecule have directions making an angle greater than $\pi/2$ with the normal to the surface, must each penetrate into the hollow between two neighbouring solid molecules and suffer a second encounter with one of them under conditions which necessitate its taking up on the average any motion that the surface has parallel to itself.

Now suppose that on the average the molecules of gas which collide with the solid come a distance $\lambda/2$ since their last collision with molecules of gas; then their average distance normally from the surface at the instant of last collision with their fellows will be the average distance of a hemisphere of radius $\lambda/2$ from its base, which is $\lambda/4$, and thus the molecules of gas which collide with the solid, which is fixed, reach it with a relative molar velocity $\lambda dw/dx 4$; but after the collision only the fraction f retain this, so that the gas in contact with the solid surface may be said to retain as a whole the velocity $f\lambda dw/dx 4$, which constitutes a velocity of

slipping, and shows how slipping arises, but does not give its amount correctly ; this, however, can soon be obtained. Let w_1 be the sudden change of velocity on passing from solid to gas ; then the $\lambda dw/dx$ just given must be increased by w_1 , and then the average loss of momentum experienced by a molecule encountering the fixed surface is $m(f\lambda dw/dx + w_1)$; but the number encountering unit surface in unit time is (2) $nv/4$, and therefore the frictional force exerted by unit surface of solid on the gas is $nmv(f\lambda dw/dx + w_1)/4$, which is equal to $\eta dw/dx$, the friction on parallel unit surface in the gas when the motion is steady : thus

$$w_1 = \frac{dw}{dx} \left(\frac{4\eta}{nmv} - \frac{f\lambda}{4} \right) ; \quad . \quad . \quad . \quad . \quad . \quad (8)$$

but $\eta = .365 nmv\lambda$ or, working with the same methods of approximation as we have been using, $\eta = nmv\lambda/4$, and then

$$w_1 = \frac{dw}{dx} \lambda (1 - f/4) . \quad . \quad . \quad . \quad . \quad (9)$$

f is a fraction which from its nature is unlikely to exceed $1/2$, so that we can write $w_1 = a\lambda dw/dx$ with the knowledge that a is not much different from unity. At both the moving and the fixed surfaces there is this discontinuity of amount w_1 , so that in the theory of viscosity, instead of writing $dw/dx = w/D$ for the steady state, we must write

$$\frac{dw}{dx} = \frac{w - 2w_1}{D}, \quad \therefore \quad \frac{dw}{dx} = \frac{w}{D(1 + 2a\lambda/D)} \quad . \quad (10)$$

$a\lambda$ or ζ is called the coefficient of slipping ; under ordinary circumstances it may be neglected, but when D is comparable with λ , as it mostly is in connexion with thermal transpiration and radiometer motion, slipping becomes of fundamental importance. When D is only a fraction of λ viscosity practically ceases, because the molecules traffic backwards and forwards between the solids with so few encounters amongst themselves that they hardly affect one another's motion, but they still exercise friction on the solids whose amount is easily calculated. Suppose that the gas between two parallel solid planes at rest is also at rest, except of course for the velocities of agitation, and then let one of the planes be set moving parallel to itself with velocity w ; then, as we have seen, the molecules colliding with it leave on the average with velocity fw , and when they reach the fixed plane a fraction f will have this velocity reduced to zero, while $1 - f$ will retain it unaltered, so that on the average the molecules

leaving the fixed surface after their first encounters with the moving and with the fixed have velocity $(1-f)fw$; but without following up this process any farther we see that it implies that when the steady state has been reached the molecules leave the moving plane with velocity w_2 and the fixed plane with an average velocity w_1 , and these must be connected by the relations

$$(1-f)w_1 + fw = w_2, \quad \text{and} \quad (1-f)w_2 = w_1;$$

whence $w_1 = w(1-f)/(2-f)$, $w_2 = w/(2-f)$,

which give $(w_1 + w_2)/2 = w/2$, as of course they ought.

Each molecule that encounters the moving plane gains momentum $m(w_2 - w_1)$ or $mwf/(2-f)$, and $nv/4$ molecules encounter unit surface in unit time, so that the friction between solid and gas is

$$F = nmv wf/4(2-f); \quad . \quad . \quad . \quad (11)$$

if $f = 1/2$ this becomes $nmvw/12$, it is a limiting value of $\eta w/D(1 + 2\zeta/D)$ when D is negligible in comparison with ζ , and it is independent of the distance between the moving and fixed planes. We see therefore that we can carry the expression $\eta/(D + 2\zeta)$ into the consideration of cases either where D is made very small or ζ very large.

The expression (11) shows that in capillary tubes whose diameters are only a fraction of the mean free path—that is with very fine tubes such as the passages of porous plates and gas at ordinary pressures, or with ordinary capillary tubes and gas at low pressures, or in any tubes at low enough pressures—the flow of gas under pressure will not obey Poiseuille's laws; indeed in a line or two we can show that (11) leads at once to Graham's laws of transpiration of gases through porous plates verified and extended by Reynolds. For if the gas is passing through a fine tube of radius R with velocity w at distance x from one end, then when the flow is steady

$$\pi R nmv wf/2(2-f) = \pi R^2 dp/dx,$$

and taking account of the conditions at the two ends of a tube of length l by suffixes 1 and 2,

$$\pi R^2 w n m = \pi R^2 w_1 n_1 m = \pi R^2 w_2 n_2 m = 2(2-f) \pi R^3 (p_2 - p_1)/lv;$$

thus the time of transpiration of unit volume measured at the pressure p_2 being $1/\pi R^2 w_2$ is $\frac{1}{2} n_2 m v l / (2-f) \pi R^3 (p_2 - p_1)$.

Now Reynolds made some experiments in which $p_2 - p_1$ was kept a constant fraction of p_2 , and therefore proportional to n_2 , under which conditions the time of transpiration should

by our last expression be constant for a given gas and all values of p_2 , which was the experimental result obtained by Reynolds; moreover if we wish to compare different gases, as at a given temperature v is proportional to $1/m^{\frac{1}{2}}$ we see that the constant time of transpiration for each gas ought to be as the square root of its molecular mass, which is Graham's well-known experimental discovery verified by Reynolds.

This digression into the properties of a gas in spaces where the linear dimensions are small compared to the free path has been made as an appendix to our consideration of slipping in order to clear up the limiting conditions towards which we tend in treating of high vacua. We can now return to thermal transpiration as we left it at (4). To secure no total flow on account of u along a tube of radius R we are to have

$$B = \pi p' R^4 (1 + 4\zeta/R)/8\eta = \pi R^2 u = -\pi R^2 v \lambda (n'/n + v'/v)/6; \quad (12)$$

but $p = nmv^2/3$, so that $p'/p = n'/n + 2v'/v$, and then

$$p' R^2 (1 + 4\zeta/R)/8\eta = -v \lambda (p'/p - v'/v)/6. \quad (13)$$

Now with the methods of approximation here employed $\eta = nmv\lambda/4$ and $p = nmv^2/3$, so that $\eta = 3\lambda p/4v$, and then

$$\frac{p'}{p} \left\{ \frac{R^2}{\lambda^2} (1 + 4\zeta/R) + 1 \right\} = \frac{v'}{v}. \quad (14)$$

As $\zeta = a\lambda$ the coefficient of p'/p is a function of only R/λ , and therefore the controlling influence of the whole phenomenon of thermal transpiration is this ratio of R to λ .

If the molecules are smooth, perfectly restitutional forceless spheres $\eta = \eta_0 v/v_0$, where η_0 and v_0 are the values of η and v at 0°C .; but with the molecules of the natural gases, on account of molecular force, the function which expresses η in terms of v is more complicated (see "Viscosity of Gases and Molecular Force," *Phil. Mag.* [5] xxxvi.). But for present purposes it will suffice to use the simple relation just given by which we can express the last differential equation in terms of p and v as the only variables thus

$$\frac{dp}{dv} \left(\frac{9R^2 v_0^2 p}{16\eta_0^2 v^4} + \frac{3ARv_0}{\eta_0 v^2} \right) + \frac{1}{p} \frac{d}{dv} - \frac{1}{v} = 0, \quad (15)$$

which can be written as

$$\frac{dp}{dv} \left(\frac{Cp}{v^4} + \frac{D}{v^2} \right) + \frac{d}{dv} \log \frac{p}{v} = 0.$$

Let α and β stand for $-\frac{D}{2C} \pm \frac{1}{2C} (D^2 - 2C)^{\frac{1}{2}}$;

then the integral of this is

$$\frac{1}{2\alpha} \log(p/v^2 - \alpha) - \frac{1}{2\beta} \log(p/v^2 - \beta) + \frac{\alpha - \beta}{\alpha\beta} \log p/v = \text{constant},$$

or with suffixes 1 and 2 to indicate the ends of the tube,

$$\frac{1}{2\alpha} \log \frac{p_1/v_1^2 - \alpha}{p_2/v_2^2 - \alpha} - \frac{1}{2\beta} \log \frac{p_1/v_1^2 - \beta}{p_2/v_2^2 - \beta} + \frac{\alpha - \beta}{\alpha\beta} \log \frac{p_1 v_2}{p_2 v_1} = 0. \quad (16)$$

But this is a very awkward form of result for comparison with the experimental data, and we shall be better served if content with an approximate solution of the differential equation obtained by putting $p' = dp/dx = (p_2 - p_1)/l$ and $v' = (v_2 - v_1)/l$, $2p = p_2 + p_1$, $2v = v_2 + v_1$, thus

$$\frac{p_2 - p_1}{p_2 + p_1} \left\{ \frac{9R^2 v_0^2 (p_2 + p_1)^2}{4\eta_0^2 (v_2 + v_1)^4} + \frac{6aRv_0 (p_2 + p_1)}{\eta_0 (v_2 + v_1)^2} + 1 \right\} = \frac{v_2 - v_1}{v_2 + v_1}. \quad (17)$$

This solution brings out at once the important point that with v_2 and v_1 fixed, that is to say, the temperatures of the two ends constant, there is a certain mean pressure $(p_2 + p_1)/2$ for which $p_2 - p_1$ has a maximum value; applying the usual condition for a maximum, we find that $p_2 - p_1$ is a maximum when $p_2 + p_1 = 2\eta_0(v_2 + v_1)^2/3Rv_0$. Before proceeding to test (17) by Reynolds's experiments, we may remark that if the mean pressure $(p_2 + p_1)/2$ is made so small that R/λ is negligible in comparison with unity, then in (14) $p'/p = v'/v$, that is $p_2/p_1 = v_2/v_1$, a result in accordance with the following common-sense argument that when the mean path of a molecule is a large multiple of the radius of the tube, the molecules of the tube have practically no influence on one another; and the number that wander in at one end during unit time being $n_1 v_1/4$ and at the other $n_2 v_2/4$, thermal transpiration will continue till these are equal, that is till $n_1 v_1 = n_2 v_2$ or $p_1/v_1 = p_2/v_2$.

So far, our theoretical treatment has related to cylindrical tubes, while in Reynolds's experiment the passages through which the gases transpire are the irregular chains of cavities in a porous plate; now to a first approximation these irregular cavities may be replaced by uniform tubes whose sectional area is equal to the average section of the cavities, but it is obvious that a better approximation to the natural cavities would be a succession of frustra of cones of length L and radii R_1 and R_2 at the end sections. The thermal transpiration through such a frustrum can be readily established from (15), for taking the origin of coordinates in one end and in the axis, then the radius at distance x along the frustrum is $R = R_1 + cx$, where c is a constant: thus for the fall of pressure

from one end of the frustrum to the other $\int \frac{dp}{dx} dx$, we have from (15)

$$\int_{R_1}^{R_2} \frac{p}{v} \frac{dv}{dx} \frac{dR}{c(AR^2 + 2BR + 1)},$$

where

$$A = \frac{9v_0^2 p^2}{16\eta_0^2 v}, \quad 2B = \frac{3av_0 p}{\eta_0 v^2},$$

which, if we regard dv/dx , p , and v as having constant average values throughout the short length L , may be written

$$\frac{p}{v} \cdot \frac{dv}{dx} \cdot \frac{1}{c} \cdot \frac{1}{2(B^2 - A)} \log \frac{R_2 A + B - (B^2 - A)^{\frac{1}{2}}}{R_2 A + B + (B^2 - A)^{\frac{1}{2}}} \cdot \frac{R_1 A + B + (B^2 - A)^{\frac{1}{2}}}{R_1 A + B - (B^2 - A)^{\frac{1}{2}}}$$

or

$$\frac{p}{v} \cdot \frac{dv}{dx} \cdot \frac{1}{c} \cdot \frac{1}{2(B^2 - A)^{\frac{1}{2}}} \log \left\{ 1 + \frac{2(B^2 - A)^{\frac{1}{2}}(R_2 - R_1)}{AR_2 R_1 + B(R_2 + R_1) + (B^2 - A)^{\frac{1}{2}}(R_1 - R_2) + 1} \right\}$$

The form of this expression suggests that we should expand the log by the approximate relation $\log(1+z)=z$, which yields

$$\frac{p}{v} \frac{dv}{dx} \frac{(R_2 - R_1)/c}{AR_2 R_1 + B(R_2 + R_1) + (B^2 - A)^{\frac{1}{2}}(R_1 - R_2) + 1}.$$

For a frustrum pointing in the opposite direction we should have to interchange R_2 and R_1 and change the sign of c , which would give us our last expression with only the sign of $R_1 - R_2$ changed in the denominator; thus for a pair of frustra oppositely directed, we get

$$2 \frac{p}{v} \frac{dp}{dv} \frac{R_2 - R_1}{c} \times \frac{1}{AR_2 R_1 + B(R_2 + R_1) + 1 - (B^2 - A)(R_1 - R_2)^2 / \{AR_2 R_1 + B(R_2 + R_1) + 1\}}; \quad (18)$$

or confining our attention to cases where $(R_1 - R_2)^2$ may be neglected, and remembering that $(R_2 - R_1) = Lc$ and that $2Ldv/dx$ is equal to the difference of velocities at the two ends of the double frustrum, we see that an approximate integral solution of the differential equation of thermal transpiration through a series of oppositely directed frustra in which R_2 and R_1 are not very different (R_2 not to exceed

$2R_1$ say) is

$$\frac{p_2 - p_1}{p_2 + p_1} = \frac{v_2 - v_1}{v_2 + v_1} \frac{1}{A'(p_2 + p_1)^2/4 + B'(p_2 + p_1)/2 + 1}, \quad (19)$$

where

$$A' = 9R_2R_1v_0^2/\eta_0^2(v_2 + v_1)^4, \\ B' = 6a(R_2 + R_1)v_0/\eta_0(v_2 + v_1)^2,$$

while for a uniform tube we have seen that the solution (17) is what this becomes when $R_2 = R_1 = R$. The simplicity of the case of frustra breaks down when R_1 becomes only a small fraction of R_2 , for then we cannot neglect $(R_2 - R_1)^2$ as we did above.

To make clear the comparison between (17) and (19) and experiment a brief description of Reynolds's arrangements is necessary: imagine a cylinder divided into five compartments by planes perpendicular to its axis, the middle one filled by a plate of porous material, those on each side of it made into small gas-holders connectable with gas supply and manometers and separated from the end chambers by metal plates, the end chambers being intended to act as a sort of jacket to each of the gas-holders, the one having a stream of steam carried through it and the other a stream of cold water. When a stationary state of temperature is established along the cylinder, the two faces of the porous plate come to fixed temperatures θ_2 and θ_1 , corresponding to the molecular velocities v_2 and v_1 , and the gas transpires from the cooler face of the plate to the hotter, till the pressures become p_2 and p_1 as given by the equation. The internal diameter of the cylinder was 38 mm. and the thickness of the porous plates varied from 1.5 to 14.2 mm., the materials being meerschaum and stucco. Reynolds gives the temperatures of the two jacket-chambers, but not those of the faces of the porous plate, which are the ones we require; we will show afterwards how to obtain these approximately, but for the present it suffices to know that in any one series of experiments v_2 and v_1 remained constant, while the mean pressure $(p_2 + p_1)/2$ in the passages of the porous plate varied from about 760 mm. of mercury down to about 4. From any three sets of values of $p_2 - p_1$ and $(p_2 + p_1)/2$ for any gas, it is possible by equation (19) to calculate $(v_2 + v_1)/(v_2 - v_1)$ and A' and B' , or from the whole series of measurements mean values of these can be calculated, and then at all mean pressures $p_2 - p_1$ can be calculated for comparison with the experimental values.

For Reynolds's meerschaum plate II., having a thickness of 6.3 mm. and with the temperature of the steam-jacket at 100° C. and that of the water-jacket at 8° , the values of the

parameters in (19) are, with the mm. of mercury as unit of pressure,

	$(v_2+v_1)/2(v_2-v_1)$	B'	A'
Air	16	·0094	0·0
H ₂	12	·0022	0·0
CO ₂	16	·012	0·0 ₅ <i>i. e.</i> ·000005

These give the following comparison :—

Air	$(p_2+p_1)/2$...	764	328	217	94·0	50·8	23·1	12·7
	p_2-p_1 cal. ...	5·9	5·0	4·4	3·1	2·2	1·2	·7
	p_2-p_1 exp. ...	6·1	5·1	4·3	3·0	2·0	1·1	·9
H ₂	$(p_2+p_1)/2$...	767	330	190	108	50·8	25·4	12·7
	p_2-p_1 cal. ...	23·8	16·0	11·2	7·3	3·8	2·0	1·0
	p_2-p_1 exp. ...	23·4	15·2	11·2	7·1	3·8	2·0	·9
CO ₂	$(p_2+p_1)/2$...	764	495	362	267	203	114	50·8
	p_2-p_1 cal. ..	3·7	3·8	3·8	3·7	3·5	2·9	2·0
	p_2-p_1 exp. ...	3·3	4·1	4·1	3·8	3·3	2·8	2·0

With the meerschaum plate III., having a thickness of 11·2 mm. and with the jackets at 100° and 17·6°, the parameters are :—

	$(v_2+v_1)/2(v_2-v_1)$	B'	A'
Air	18	·0094	0·0
H ₂	16·6	·00181	0·0

whence the comparison

Air	$(p_2+p_1)/2$...	787	698	508	317	209	198	86·4
	p_2-p_1 cal. ...	5·2	5·1	4·8	4·1	3·9	3·8	2·7
	p_2-p_1 exp. ...	5·6	5·4	5·4	4·4	3·7	3·4	2·3
Air	$(p_2+p_1)/2$...	50·8	35·6	21·1	10·2	7·11	4·82	3·81
	p_2-p_1 cal. ...	1·9	1·5	1·0	·52	·37	·26	·20
	p_2-p_1 exp. ...	1·6	1·3	1·0	·63	·49	·37	·39
H ₂	$(p_2+p_1)/2$...	864	762	470	290	193	121	76·2
	p_2-p_1 cal. ...	20·3	19·2	15·3	11·5	8·6	6·0	4·0
	p_2-p_1 exp. ...	20·1	19·5	15·9	11·7	8·0	5·6	4·0
H ₂	$(p_2+p_1)/2$...	43·2	27·9	25·4	16·5	15·3	8·13	
	p_2-p_1 cal. ...	2·4	1·6	1·46	·96	·90	·48	
	p_2-p_1 exp. ...	2·7	1·6	1·68	·82	·96	·58	

With the stucco plate I., having a thickness of 6·3 mm. and with the temperatures of the jackets at 100° and 18°·4 (17° for H₂), the parameters are :—

	$(v_2+v_1)/2(v_2-v_1)$	B'	A'
Air	20	·045	·045
H ₂	18	·00917	·0561

which furnish the comparison

Air	$\left\{ \begin{array}{l} (p_2+p_1)/2 \dots \\ p_2-p_1 \text{ cal. } \dots \\ p_2-p_1 \text{ exp. } \dots \end{array} \right.$	$\left\{ \begin{array}{l} 757 \\ \cdot 59 \\ \cdot 56 \end{array} \right.$	$\left\{ \begin{array}{l} 594 \\ \cdot 66 \\ \cdot 63 \end{array} \right.$	$\left\{ \begin{array}{l} 564 \\ \cdot 67 \\ \cdot 67 \end{array} \right.$	$\left\{ \begin{array}{l} 288 \\ \cdot 79 \\ \cdot 88 \end{array} \right.$	$\left\{ \begin{array}{l} 131 \\ \cdot 85 \\ \cdot 92 \end{array} \right.$	$\left\{ \begin{array}{l} 88\cdot 9 \\ \cdot 82 \\ \cdot 83 \end{array} \right.$
	$\left\{ \begin{array}{l} (p_2+p_1)/2 \dots \\ p_2-p_1 \text{ cal. } \dots \\ p_2-p_1 \text{ exp. } \dots \end{array} \right.$	$\left\{ \begin{array}{l} 59\cdot 7 \\ \cdot 77 \\ \cdot 74 \end{array} \right.$	$\left\{ \begin{array}{l} 31\cdot 7 \\ \cdot 64 \\ \cdot 58 \end{array} \right.$	$\left\{ \begin{array}{l} 15\cdot 2 \\ \cdot 45 \\ \cdot 38 \end{array} \right.$	$\left\{ \begin{array}{l} 6\cdot 35 \\ \cdot 24 \\ \cdot 20 \end{array} \right.$	$\left\{ \begin{array}{l} 3\cdot 84 \\ \cdot 17 \\ \cdot 17 \end{array} \right.$	
	$\left\{ \begin{array}{l} (p_2+p_1)/2 \dots \\ p_2-p_1 \text{ cal. } \dots \\ p_2-p_1 \text{ exp. } \dots \end{array} \right.$	$\left\{ \begin{array}{l} 858 \\ 3\cdot 56 \\ 3\cdot 40 \end{array} \right.$	$\left\{ \begin{array}{l} 686 \\ 3\cdot 75 \\ 3\cdot 65 \end{array} \right.$	$\left\{ \begin{array}{l} 508 \\ 3\cdot 91 \\ 3\cdot 89 \end{array} \right.$	$\left\{ \begin{array}{l} 406 \\ 3\cdot 94 \\ 3\cdot 89 \end{array} \right.$	$\left\{ \begin{array}{l} 339 \\ 3\cdot 92 \\ 3\cdot 90 \end{array} \right.$	$\left\{ \begin{array}{l} 249 \\ 3\cdot 78 \\ 3\cdot 82 \end{array} \right.$
H ₂	$\left\{ \begin{array}{l} (p_2+p_1)/2 \dots \\ p_2-p_1 \text{ cal. } \dots \\ p_2-p_1 \text{ exp. } \dots \end{array} \right.$	$\left\{ \begin{array}{l} 203 \\ 3\cdot 62 \\ 3\cdot 73 \end{array} \right.$	$\left\{ \begin{array}{l} 152 \\ 3\cdot 35 \\ 3\cdot 35 \end{array} \right.$	$\left\{ \begin{array}{l} 82\cdot 5 \\ 2\cdot 55 \\ 2\cdot 64 \end{array} \right.$	$\left\{ \begin{array}{l} 50\cdot 8 \\ 1\cdot 91 \\ 1\cdot 93 \end{array} \right.$	$\left\{ \begin{array}{l} 17\cdot 8 \\ \cdot 85 \\ \cdot 84 \end{array} \right.$	$\left\{ \begin{array}{l} 7\cdot 62 \\ \cdot 40 \\ \cdot 40 \end{array} \right.$

These comparisons show that the equation (19) represents the facts of thermal transpiration, for the discrepancies between calculation and experiment are mostly of the same order as the experimental uncertainty, as can be seen from a careful comparison of the experimental data amongst themselves.

We have now to consider the relation between the experimental values of the parameters $(v_2+v_1)/2(v_2-v_1)$, B', and A' and their theoretical natures. First, as to $(v_2+v_1)/2(v_2-v_1)$, which is equal to $(\theta_2^{\frac{1}{2}}+\theta_1^{\frac{1}{2}})/2(\theta_2^{\frac{1}{2}}-\theta_1^{\frac{1}{2}})$ where θ_2 and θ_1 are the temperatures of the two faces of the porous plate; now the walls between the jackets and the air-chambers are of thin metal, and the chambers are of the same shape and size, so that the mean of the temperatures θ_2 and θ_1 must be nearly equal to that of the two jacket temperatures i_2 and i_1 ; thus $\theta_2+\theta_1=i_2+i_1$, which, with the values given for $(v_2+v_1)/2(v_2-v_1)$, suffices to determine θ_2 and θ_1 .

		Air.	H ₂ .	CO ₂ .
Meerschäum II. . .	$\left\{ \begin{array}{l} \theta_2-273 \\ \theta_1-273 \end{array} \right.$	$\left\{ \begin{array}{l} 74 \\ 34 \end{array} \right.$	$\left\{ \begin{array}{l} 81 \\ 27 \end{array} \right.$	$\left\{ \begin{array}{l} 74 \\ 34 \end{array} \right.$
Meerschäum III. . .	$\left\{ \begin{array}{l} \theta_2-273 \\ \theta_1-273 \end{array} \right.$	$\left\{ \begin{array}{l} 77 \\ 40\cdot 5 \end{array} \right.$	$\left\{ \begin{array}{l} 79 \\ 39 \end{array} \right.$	
Stucco I.	$\left\{ \begin{array}{l} \theta_2-273 \\ \theta_1-273 \end{array} \right.$	$\left\{ \begin{array}{l} 76 \\ 42\cdot 5 \end{array} \right.$	$\left\{ \begin{array}{l} 77 \\ 40 \end{array} \right.$	

The temperatures θ_2 and θ_1 are determined by the flow of heat from the thin metal wall of the hot jacket to that of the cold one, by conduction along the rubber walls of the cylinder, by radiation across the two gas-chambers, by convection-currents in the gas-chambers, and also by conduction through the gas of the chambers, but the conductivity of gases is so small compared to that of even badly-conducting solids, that the direct effect of gaseous conduction may be neglected, although the indirect effect of the conductivity of the gas in determining the amount of heat carried by convection may be appreciable, as would appear to be the case with hydrogen and meerschaum plate II. It would be possible to make a rough calculation as to what θ_2 and θ_1 ought to be according to the theory of conduction, but Reynolds states that the condition of the radiating surfaces and the sizes of the chambers were altered during the experiments, so that it is not worth while to do more than notice that the values obtained for the temperatures of the faces of the porous plates are consistent in a general way with what we should expect from the temperatures of the jackets, the thickness of the gas in the two chambers which was about 5 mm., and the given thicknesses of the plates.

As to the values of B' , which stands for

$$6av_0(R_2 + R_1)/\eta_0(v_2 + v_1)^2;$$

since mv^2 is proportional to θ , and $(\theta_2^{\frac{1}{2}} + \theta_1^{\frac{1}{2}})^2$ is nearly the same in all the experiments, we should expect $B'\eta_0/m^{\frac{1}{2}}$ to be constant for different gases with the same plate, and proportional to the mean radius of the passages in the plate; thus, using the viscosities as obtainable from Graham's experiments in terms of that for oxygen as unity, and the molecular masses in terms of that of hydrogen as 2, we have:—

	H ₂ .	Air.	CO ₂ .
m . . .	2	28·8	44
η_0 . . .	·44	·90	·755

which give the following values of $10^5 B'\eta_0/m^{\frac{1}{2}}$:—

	H ₂ .	Air.	CO ₂ .
Meerschaum II. . . .	68	158	137
Meerschaum III. . . .	56	158	
Stucco	285	755	

This shows that the values yielded by hydrogen, instead of being equal to those given by air, are between $\frac{1}{2}$ and $\frac{1}{3}$ of them, a discrepancy whose cause will be found immediately; but it is to be noted that while the results for hydrogen

make the mean radius of the passages in stucco 4·2 and 5·1 times those in meerschäum II. and III., those for air make it 4·8 and 4·8 times, and the agreement of the means 4·65 and 4·8 is close enough to show that our expression

$$6av_0(R_2 + R_1)/\eta_0(v_2 + v_1)^2$$

is right enough as regards the occurrence of the mean radius of the passages in it; and moreover our equation (14) showed that R entered in the form R/λ , so that the discrepancy just found must be due to some considerations being ignored in connexion with λ .

Now it is a well known fact established by experiment that gases are condensed in the passages of porous bodies. The condensing action exerted by a solid surface on a gas is easily expressed quantitatively, for near the end of section (8) of my paper on the Laws of Molecular Force (*Phil. Mag.* [5] xxxv.) the attraction of a cylinder of radius c , length h , and density ρ on a particle of mass m at distance z along the axis from the nearest end, the law of force being $3Am\rho/r^4$, is

$$2A\pi m\rho[1/z - 1/(z+h) - 1/(c^2+z^2)^{\frac{1}{2}} + 1/\{c^2+(z+h)^2\}^{\frac{1}{2}}],$$

whence the attraction on a particle at small distance z from the surface of a solid may be written $2A\pi m\rho/z$, and if the particle is one of the molecules of a gas, the condition of equilibrium in the gas is

$$-dp/dz = 2A\pi\rho nm/z \quad \text{or} \quad -dp/p = 6A\pi\rho dz/zv^2;$$

and if p_s is the pressure in the layer nearest to the surface which is at distance z_s from the surface, and p_c is the pressure at a distance z_c where the effects of the solid are negligible, then

$$\log p_s/p_c = \frac{6A\pi\rho}{v^2} \log z_s/z_c, \quad . \quad . \quad . \quad (20)$$

a formula which makes the density of the gas in contact with the solid nearly proportional to the density where the gas is free, because with gases $6A\pi\rho/v^2$ is a small fraction. This formula will be investigated a little further in my next paper, on "Boyle's Law at very Low Pressures."

A rigorous investigation for condensation in a tube would be simple enough, but it suffices for our present purposes to see that in most cases the density at the surface of the tube will be connected with the density at the axis by the relation

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obtained by putting surface-density and axial density in place of p_s and p_c in the last formula.

It is easy also to obtain an expression for the average density, but as it is evident that for a given tube at a given temperature the average density remains proportional to the density at the axis, which is the same as if there was no attraction between gas and solid, we see at once that the effect of surface condensation on our investigation of thermal transpiration is to multiply the density by a factor which remains nearly constant for a given tube or to divide λ by the same factor, and the effect of ignoring this factor as we have done is to produce values of $10^3 B' \eta_0 / m^{\frac{1}{2}}$ which ought to be divided by the factor before they should be expected to be constant for any one plate. Now experiment has shown that hydrogen is much less condensed on solid surfaces than other gases, so that with hydrogen the factor will be nearly unity (probably), and therefore, from the last little table, that for air between 2 and 3; the factor for CO_2 ought to be larger still, as this gas is much more liable to surface condensation than air, while the last table would make the factor to be $137/68$ or 2; but too much reliance must not be placed on the value of B' for CO_2 , as Reynolds found the trouble caused by the condensation of the CO_2 to be so great as to discourage him from making any further experiments with it. Thus the apparent discrepancy in the last table has furnished some new evidence in connexion with condensation of gases in the passages of porous solids.

As to the values of A' , which stands for

$$9R_2R_1v_0^2/\eta_0^2 (v_2 + v_1)^4,$$

we see that as a is nearly 1 the value of $B'^2/16A'$ ought to be nearly equal to $(R_2 + R_1)^2/4R_2R_1$, and of course the value of the ratio $B'^2/16A'$ is not affected by our ignoring condensation in the establishment of the fundamental equations. In the case of hydrogen, the values of B' and A' for stucco I. lead to an unreal value of R_2/R_1 , and thus we see that the formula (19) for conical passages is too much of a refinement for present purposes; and therefore abiding by the formula (17) for cylindrical passages we may say that $B'^2/16A'$ ought to be not much different from unity. For stucco I. the values of $B'^2/16A'$ are .86 for hydrogen and 2.5 for air, while for meerschaum II. and CO_2 the value is 1.8; these values are near enough to 1.0 to give satisfactory evidence of the general soundness of the details in the theory.

Reynolds, guided by his theory, formulated his experimental

results in a number of laws, but there is no occasion for us to follow these seriatim as they are all contained in the symbolical statements of equations (17) and (14), which we have already tested by the experimental results.

An interesting result of thermal transpiration experiments is that they enable us to calculate the mean radius of the passages in porous materials, for in the case of hydrogen the measurements must be but little complicated by molecular force; thus the values given for B' in the case of hydrogen, if multiplied by 760 to pass from the mm. of mercury to the atm. as unit of pressure, and then divided by $1033\cdot3 \times 981$ to pass to the dyne per sq. cm. as absolute unit of pressure, give us the values of $12av_0R/\eta_0(v_2+v_1)^2$; now as v_2+v_1 may be taken as relating to a mean temperature of $57^\circ \text{C}.$,

$$(v_2+v_1)^2=4v_0^2\ 330/273,$$

and $v_0=184400$ cm. per sec. and $\eta_0=.00009$, while a is nearly unity; thus for the mean radius of the passages in Reynolds's meerscham II. we get $.0000112$ cm., in meerscham III. $.0000092$, or say $1/10^5$ cm. for meerscham, while for stucco I. the value is $.000047$ cm. Thermal transpiration gives no information as to the number of passages, but this could be found from a measurement of the volume of air transpired by a plate in unit time under a measured excess of pressure on one side, or by other measurements relating to transpiration under pressure such as those made by Graham and Reynolds; for the delivery of gas could be calculated as that due to N tubes of radius R , the discharge of each being calculated according to O. E. Meyer's equation given in (7). In this way thermal and pressural transpiration measurements can be made to yield a measure of the average porosity of any solid through which hydrogen can pass. By artificially altering the porosity in a series of preparations, as for instance by hardening stucco under different pressures and similar means, so that specific gravity would give a measure of relative porosity, it might be possible to find a porosity at which hydrogen just failed to pass, which would furnish an independent measure of the diameter of the hydrogen molecule.

[To be continued.]