THE TRANSPIRATION OF AIR THROUGH A PARTITION OF WATER.

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1. *Molecular Transpiration of a Gas.*—Ever since 1895 I have observed that the Cartesian diver, used in my lectures, grew regularly heavier from year to year. The possibility of such an occurrence is at hand; for the imprisoned air is under a slight pressure-excess as compared with the external atmospheric air. But this pressure gradient is apparently so insignificant as compared with the long column of water through which the flow must take place, that opportunities of obtaining quantitative evidence in favor of such transpiration seem remote. If, however, this evidence is here actually forthcoming, then the experiment is of unusual interest, as it will probably indicate the nature of the passage of a gas, molecularly, through the intermolecular pores of a liquid. It should be possible for instance to obtain comparisons between the dimensions of the molecules transferred and the channels of transfer involved.

2. *Apparatus.*—Hence on February 27, 1890, I made a series of definite experiments[1] sufficiently sensitive that in the lapse of years one might expect to obtain an issue. The swimmer was a small light balloon-shaped glass vessel, *vd*, Fig. 1, unfortunately with a very narrow mouth, 2 mm. in diameter, at *d,* in the long column of water *A*. The small opening however gave assurance that the air would not be accidentally spilled in the intervening years. For this reason it was temporarily retained, the purpose being that of getting a safe estimate of the conditions under which flow takes place.

In Fig. 1 *ab* is a rubber hose filled with water, terminating in the receiver *R*. Here the lower level of water may be read off. Moreover *R* is provided with an open hose *C*, through which pressure or suction may be applied by the mouth, for the purpose of raising or

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[1] *Am. Journ. of Sci.*, IX., 1900, pp. 397–400.

lowering the swimmer, vd, in the column A. In this way constancy of temperature is secured throughout the column.

3. *Barometer.*—The apparatus is obviously useful for ordinary barometric purposes, and provided the temperature, t, of the air
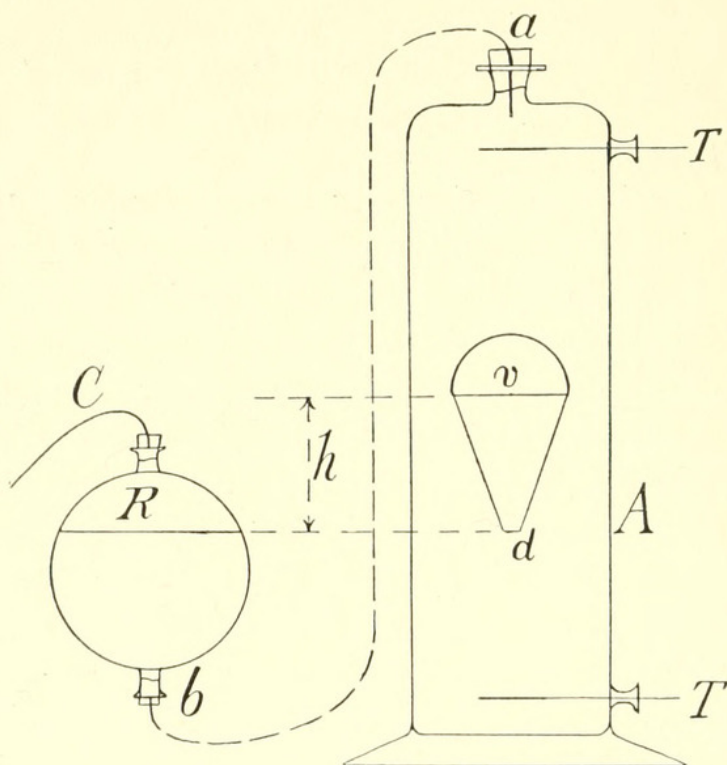

FIG. 1. Swimmer and appurtenances.

at v, is known to .025° C., the barometric height should be determinable as far as .1 mm. Apart from this the sensitiveness of the apparatus is surprising. Care must be taken to avoid adiabatic changes of temperature, so that slow manipulation is essential. These and other precautions were pointed out in the original paper (*l. c.*)

4. *Equations. Manipulation.*—Let h be the difference of level of the imprisoned water and the free surface in the reservoir R. Then it follows easily that

$$ h + H \frac{\rho_m}{\rho_w} = \frac{Rm}{gM} \frac{\tau}{(1 + m/M) - \rho_w/\rho_g}, \tag{1} $$

where H is the corrected height of the barometer (from which the mercury head equivalent to the vapor pressure of water is to be

deducted), ρ_m, ρ_w, ρ_g, the densities of mercury ($0°$ C.), water ($t°$ C.), and glass, respectively, m the mass of the imprisoned air at v, R its gas constant, and $\tau = t + 273°$ its absolute temperature. M is the mass of the glass of the swimmer and g the acceleration of gravity.

The equilibrium position of the swimmer is unstable. To find it, R may be raised and lowered for a fixed level of the swimmer; or R may be clamped and the proper level of the swimmer determined by suction and release at C. The dropping of the swimmer throughout
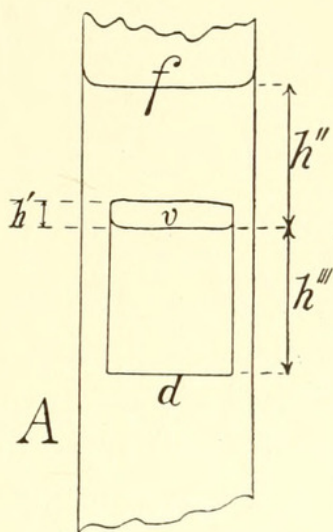
FIG. 2. Cylindrical Swimmer.

the column of water may occasion adiabatic change of temperature of .23°. It was my practice to use the latter method and to indicate the equilibrium position of the swimmer by an elastic steel ring, encircling A. In this way the correct level may be found to about 1 mm., and afterwards read off on the cathetometer.

After making the observations, the hose ab is to be separated at a, so that the swimmer falls to a support some distance above the bottom, admitting of free passage for diffusion. Clearly this diffusion is due to the difference of level, h'', between the water level in v and at the free surface of the liquid, f (see Fig. 2). Increase of barometric pressure has no differential effect. A large head h'' however means a longer column for diffusion.

5. *Data.*—In the following summary a few of the data made in 1900 are inserted, chosen at random.

In the intermediate time, I did not return to the measurements until quite recently (January, 1911), when a second series of observations was made. As much as one fourth of the air contained in 1900 had now, however, escaped, in consequence of which the above method had to be modified and all heads measured in terms of mercury. Hence if H denotes the height of the barometer diminished by the head equivalent to the vapor pressure of water, and if m/M be neglected in comparison with 1 (about .06 per cent.) the equation becomes

$$m = \frac{Mg\rho_m}{R} \frac{H(1/\rho_m - 1/\rho_g)}{\tau} \qquad (2)$$

in which the first factor of the right-hand member is constant. If the observations are made at the instant the swimmer sinks from the free surface in A, Fig. 2, H must be increased by the mercury equivalent of the height h' of v. The table contains all the data reduced to mercury heads. $A = Mg\rho_m/R$. Consequently $1{,}842 \times 10^{-6}$ grams of the imprisoned air escaped in the intervening 10.92 years; i. e., .265 of the original mass of air. In other words 168.7×10^{-6} grams per year, $.462 \times 10^{-6}$ grams per day, or 5.35×10^{-12} grams of dry air per second.

6. *Conditions of Flow.*—It is now necessary to analyze the above experiment preparatory to the computation of constants. The mouth of the swimmer had an area of but .0314 cm.^{2} When sunk the head of water above the surface v was $h'' = 24$ cm. The column of water between v and d was $h''' = 8$ cm. Hence the length of column within which transpiration took place was $24 + 2 \times 8 = 40$ cm. The right section of this column is taken as .0314 cm.^{2} throughout. Naturally such an assumption, accepted in the absence of a better one, is somewhat precarious; but it may be admitted, inasmuch as the pressure of the gas sinks in the same proportion in which the breadth of the channel enlarges. Thus there must be at least an approximate compensation. In more definite experiments a cylindrical swimmer whose internal area is the same as the annular area without will obviate this difficulty (see Fig. 2).

The pressure difference urging the flow of air from v is

$$\Delta p = 24 \times .997 \times 981 = 23470 \text{ dynes/cm.}^2$$

Hence per dyne/cm.² per sec.

$$\frac{10^{-12} \times 5.346}{10 \times 2.347} = 10^{-16} \times 2.28$$

grams of air escape from the swimmer.

A few comparisons with a case of viscous flow may here be interesting. Using Poiseuille's law in the form given by O. E. Meyer and Schumann's data for the viscosity of air, it would follow that but $.194 \times 10^{-6}$ cm.² of the $.0314$ cm.² of right section at d is open to intermolecular transpiration. The assumption of capillary transpiration is of course unwarrantable and the comparison is made merely to show that relatively enormous resistances are in question. Again the coefficient of viscosity

$$\frac{\eta}{1 + 4\xi/r} = \frac{t}{m} \frac{\pi}{16} \frac{r^4}{lR\tau}(P^2 - p^2)$$

may be determined directly. In this equation m is the number of grams of air transpiring in t seconds through the section πr^2 and in virtue of the pressure gradient $(P - p)/1$, when η is the viscosity and ξ the slip of the gas. Hence the value $\eta/(1 + 4\xi/r) = 4.8 \times 10^6$ would have to obtain, a resistance, which would still be enormously large relative to the viscosity of air $(\eta = 180 \times 10^{-6})$, even if the part of the section of the channel which is open to capillary transpiration is a very small fraction.

7. *The Coefficients of Transpiration.*—To compute the constants under which flow takes place the concentration gradient dc/dl may be replaced either by a density gradient $d\rho/dl$ or a pressure gradient dp/dl. If the coefficients in question be k_ρ and k_p respectively

$$k_p = \frac{k_\rho}{R\tau} = \frac{m}{adp/dl} \tag{3}$$

where a is the section taken equal to the area of the mouth of the swimmer, R is the absolute gas constant, τ the absolute temperature of the gas, and m the loss of imprisoned air in grams per second. If $v = mR\tau/p$ is the corresponding loss of volume at τ and p

$$k_p = \frac{k_\rho}{R\tau} = \frac{pv}{aR\tau \, dp/dl} . \tag{3'}$$

If in equation (3) the full value of m is inserted and t denotes current time, or $\dot{m} = m/t$; if

$$\frac{dp}{dl} = \frac{h''\rho_w g}{h'' + 2h'''}$$

where ρ_w is the density of water, h'' and h''' the difference of level (see Fig. 2) of the surface in v below the free surface in A and above the mouth at d, the relations are

$$k_p = \frac{M\rho_m}{Rt} \frac{H}{\tau} \frac{1 + 2h'''/h''}{a\rho_w} (1/\rho_w - 1/\rho_g), \tag{4}$$

$$k_\rho = k_p R\tau . \tag{5}$$

The acceleration of gravity, g, has dropped from both equations; k_ρ is independent of $R\tau$. The coefficient k_p, however, is more perspicuous.

If h''' is made very small in comparison with h'' (care being taken to avoid loss of air during manipulation) h'' will also vanish; or for $h'' = 0$

$$k_p = \frac{M\rho_m}{tRa\rho_w} \frac{H}{\tau} (1/\rho_w - 1/\rho_g), \tag{6}$$

and similarly for $h'' = 0$

$$\dot{m} = k_p a\rho_w g \frac{1}{1 + 2h'''/h''}$$

reduces to

$$\dot{m} = k_v a\rho_w g .$$

Thus the apparatus is most sensitive if a is as large as possible and h'''/h'' as small as possible and the length of the column in A is eventually without influence on the result. Hence if for a cylindrical swimmer the internal right section is equal to the area of the annular space between the outer wall of the swimmer and the inner wall of the vessel A, if the column of water above the swimmer is removed during the prolonged intervals of time between observations, the

section a through which capillary transpiration takes place is definitely given. It is obvious that the swimmer must be suspended, for instance by fine cross wires, above the bottom of the tank A.

Reference is finally to be made to convection and to temperature. The manipulation during observation necessarily stirs up the water and distorts the regular pressure gradient. Hence observations are to be made rarely. Again to obviate convection in general the vessel must be kept in a room of nearly constant temperature.

8. *Values of the Coefficients.*—If the data of the above summary be inserted in the equations for k_p and k_ρ,

$$k_\rho = \frac{\dot{m}R\tau}{a\,dp/dl} = \frac{5.35 \times 10^{-12} \times 2.87 \times 10^6 \times 298}{10314 \times 23470/40} = 250 \times 10^{-6},$$

$$k_p = k_\rho/R\tau = .29 \times 10^{-12}.$$

Hence for a gradient of 1 dyne per cm., 2.9×10^{-13} grams of air flow between opposed faces of a cu. cm. of water per second. This may be put roughly as about 2.4×10^{-10} cu. cm. of air per second. The speed of migration of individual air molecules intermolecularly through a wall of water is thus 2.4×10^{-10} cm./sec. for a dyne/cm. gradient.

Since the gradient is the energy expended when the cu. cm. is transferred 1 cm. along the channel and if the number of air molecules per cu. cm. be taken as $N = 60 \times 10^{18}$, the force acting per molecule to give it the velocity just specified is $1/(60 \times 10^{18})$ dynes. Hence the force or drag per molecule if its speed is to be 1 cm. per sec. is

$$f = \frac{1}{2.4 \times 10^{-10}} \frac{1}{60 \times 10^{18}} = \frac{1}{144 \times 10^8}\,\text{dynes}$$

$$f = 6.9 \times 10^{-11}\ \text{dynes, if } v = \text{cm./sec.}$$

This may be compared with the force necessary to move a small sphere through a very viscous liquid of viscosity η. This force is

$$f = 6\pi\eta r v.$$

If $v = 1$ cm./sec., $2r = 10^{-8} \times 2$ cm. the diameter of the sphere of influence of a molecule, and $f = 6.9 \times 10^{-11}$ dynes the value just found,

$$\eta = \frac{6.9 \times 10^{-11}}{6\pi \times 10^{-8}} = 366 \times 10^{-6}.$$

In other words the molecule moves through a liquid about twice as viscous as the air itself.

9. *Conclusion.*—The above data are subject to the different hypotheses stated; but it has been shown that the results may be obtained by the method described free from ulterior assumption. It seems to me that detailed investigations of the above kind carried on with reference to both the chemical and the physical properties of the liquid, *i. e.,* with different liquids and different gases at different temperatures and pressures, cannot but lead to results of importance bearing on the molecular physics involved. Hence experiments of this kind have been begun in this laboratory and I hope to report the results from time to time. Obviously in a doubly closed water manometer (U-tube) the unequal heads of the two columns of liquid must in a way similar to the above vanish in the lapse of time. This method seems particularly well adapted to obviate convection. Finally hydrogen shows a measurable amount of molecular transpiration in the daily march of results already obtained, and with this gas a new and direct method for obtaining the molecular diameter is foreshadowed.

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