



LII. On the distribution of a gas in an electrical field

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those calculated from my measurements ; in the second and third those found by Olszewski and Estreicher. Those given as Estreicher's are obtained by giving weight to his intermediate points, as explained above.

The values of the vapour-pressures of oxygen and nitrogen were introduced into the equation $r' \text{ gas} = r \times \frac{P_0}{P_n}$, but were not found to satisfy it, nor does the introduction of a constant factor improve it, as may be seen from the subjoined table, the last column of which expresses the ratio $\frac{r'}{r} \frac{P_0}{P_n}$.

T.	r' .	r .	$\frac{P_0}{P_n}$.	$\frac{r'}{r}$.	
80	·1364	·5004	·2174	·2725	1·254
82	·3089	1·090	·2240	·2832	1·264
84	·5835	1·959	·2322	·2979	1·283
86	1·092	3·505	·2388	·3116	1·305
88	2·290	7·065	·2480	·3241	1·307
90	8·806	24·97	·2560	·3525	1·377

There does not appear, therefore, to be any connexion between the ratio of the vapour-pressures and the composition of the gaseous phase in the distillation of oxygen and nitrogen at constant pressure ; it would be better, however, for this purpose to investigate the distillation at constant temperature, and this it is proposed to do.

I have to express my cordial thanks to Professor Ramsay, at whose suggestion the work was begun, and who has shown great personal interest during the investigation; and especially am I indebted to Dr. F. G. Donnan for the valuable help he has given me at various times.

University College, London,
February 1900.

LII. *On the Distribution of a Gas in an Electrical Field.*
By GEORGE W. WALKER, B.A., A.R.C.Sc., Sir Isaac Newton Student in the University of Cambridge*.

THIS paper forms part of an essay on the kinetic theory of gases, at which I have been working for some time. The essay will not be published for some time yet ; but on account of the interest of the above question it seems desirable to publish the results at which I have arrived.

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For the sake of generality we shall suppose that the number of free positive atoms in unit volume is n_1 , the number of free negative atoms n_2 , and the number of molecules N . These are averages and do not imply that the atoms which constitute the set n_1 are the same at every instant, but that we have reached a state in which the number of molecules which disintegrate is equal to the number formed by recombination. We shall regard the molecule as consisting of a pair of atoms in contact, each of mass m and radius a , and one carrying a positive charge e , and the other a negative charge $-e$.

We consider first the case in which the gas as a whole is at rest.

Let χ be the electrical potential and R the resultant force at a point.

Then Boltzmann's extension of Maxwell's distribution law gives at once

$$\begin{aligned} n_1 &= N_1 e^{-he\chi}, & n_2 &= N_2 e^{+he\chi}, \\ N &= -A \int_{+1}^{-1} e^{-2eah \frac{\partial \chi}{\partial v} \cos \vartheta} \delta \cos \vartheta \\ &= A \frac{\sinh 2eah \frac{\partial \chi}{\partial v}}{eah \frac{\partial \chi}{\partial v}}, \end{aligned}$$

where $\cos \vartheta$ is the angle which the axis of a molecule makes with the direction of R , *i. e.* $-\frac{\partial \chi}{\partial v}$; h is the usual constant in the kinetic theory and is inversely proportional to the temperature.

We shall first show that these distribution laws satisfy the conditions of hydrostatic equilibrium.

If p be the pressure we get

$$p = \frac{n_1}{h} + \frac{n_2}{h} + \frac{N}{h},$$

which is Dalton's law of partial pressures.

Consider for the moment that χ depends only on one coordinate, x . Then we must have

$$\frac{\partial p}{\partial x} = X,$$

where X is the bodily force acting on all the atoms and molecules in unit volume.

For the free positive atoms

$$X_1 = -en_1 \frac{\partial \chi}{\partial x} = \frac{1}{h} \frac{\partial n_1}{\partial x}.$$

For the free negative atoms

$$X_2 = en_2 \frac{\partial \chi}{\partial x} = \frac{1}{h} \frac{\partial n_2}{\partial x}.$$

For the molecules

$$\begin{aligned} X_3 &= +A2ea \frac{\partial^2 \chi}{\partial x^2} \int_{+1}^{-1} e^{-2eah \frac{\partial \chi}{\partial x} \cos \vartheta} \cos \vartheta \delta \cos \vartheta \\ &= \frac{1}{h} \frac{\partial N}{\partial x}. \end{aligned}$$

Thus the equation of hydrostatic equilibrium is identically satisfied.

Let ρ be the electrical density, then

$$\begin{aligned} \frac{\partial^2 \chi}{\partial x^2} &= -4\pi\rho, \\ \rho &= en_1 - en_2 - \frac{\partial I}{\partial x}, \end{aligned}$$

where I is the intensity of electrification due to the molecules. It is sufficient to retain only squares of ea in calculating I , and there is little difficulty in showing that

$$\frac{\partial I}{\partial x} = -\frac{4}{3} N_0 ha^2 e^2 \frac{\partial^2 \chi}{\partial x^2}$$

where N_0 is the number of molecules in unit volume at a part of the field where $\frac{\partial \chi}{\partial z}$ is zero.

Hence

$$\frac{\partial^2 \chi}{\partial x^2} = 4\pi e(N_2 e^{ehx} - N_1 e^{-hex}) - \frac{16\pi}{3} N_0 ha^2 e^2 \frac{\partial^2 \chi}{\partial x^2}.$$

In general the equation is

$$\left(1 + \frac{16\pi}{3} N_0 ha^2 e^2\right) \nabla^2 \chi = 4\pi e(N_2 e^{ehx} - N_1 e^{-ehx}).$$

We see that the effect of the molecules is simply to increase the specific inductive capacity, so that

$$K = 1 + \frac{16\pi}{3} N_0 ha^2 e^2.$$

I do not propose to discuss this value of K here. Suffice it to say that with the usual estimates of $N_0 h$ and a it gives very nearly Professor J. J. Thomson's value of e calculated

from the electrochemical equivalent. K for a gas is, however, so nearly 1 that we may take it as 1 without vitiating our results.

The equation for χ is then

$$\nabla^2 \chi = 4\pi e(N_2 e^{eh\chi} - N_1 e^{-eh\chi}).$$

In this general form little can be done with the equation; but when χ depends only on x we can obtain the complete integral

$$\frac{\partial^2 \chi}{\partial x^2} = 4\pi e(N_2 e^{eh\chi} - N_1 e^{-eh\chi}).$$

Multiply by $\frac{\partial \chi}{\partial x}$ and integrate,

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h} \left\{ N_2 e^{eh\chi} + N_1 e^{-eh\chi} - B \right\}$$

where B is an arbitrary constant.

This may be rewritten

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h} \sqrt{N_1 N_2} \left\{ 2 \cosh(eh\chi + \alpha) - \frac{B}{\sqrt{N_1 N_2}} \right\},$$

where $\epsilon^{2\alpha} = \frac{N_2}{N_1}$.

Put $\cosh\left(\frac{eh\chi + \alpha}{2}\right) = y$,

and we get

$$\left(\frac{dy}{dx}\right)^2 = 2\pi h e^2 \sqrt{N_1 N_2} \{1 - y^2\} \left\{ 2 + \frac{B}{\sqrt{N_1 N_2}} - 4y^2 \right\}.$$

Thus

$$\cosh \frac{eh\chi + \alpha}{2} = \text{sn}(\lambda x + \beta, k)$$

where

$$\lambda^2 = 2\pi h e^2 \sqrt{N_1 N_2} \left\{ 2 + \frac{B}{\sqrt{N_1 N_2}} \right\}$$

$$k^2 = \frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}}, \quad \text{if } \frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}} < 1,$$

and β is an arbitrary constant.

If $\frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}}$ is > 1 ,

we get

$$\cosh \frac{eh\chi + \alpha}{2} = \frac{1}{\operatorname{sn}(\lambda x + \beta, k)}$$

where

$$\lambda^2 = 8\pi h e^2 \sqrt{N_1 N_2},$$

$$k^2 = \frac{B}{2 + \frac{B}{\sqrt{N_1 N_2}}}.$$

Before discussing the nature of the solution we shall consider the case when an electric current is passing. We shall suppose that the current is due to the bodily transference of the free atoms, while the molecules have practically no bodily motion.

Fixing our attention for the moment on the positive group:—

Let p_1 be the pressure, ρ_1 the density, so that $p_1 = \frac{\rho_1}{hm}$, and let u_1 be the group velocity. Then the hydrodynamical equations are

$$\frac{\partial u_1}{\partial t} + u_1 \frac{\partial u_1}{\partial x} = -\frac{1}{hm} \frac{\partial \log \rho_1}{\partial x} - \frac{e}{m} \frac{\partial \chi}{\partial x}$$

and

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial}{\partial x} \rho_1 u_1 = 0.$$

For a steady state

$$\frac{\partial \rho_1}{\partial t} = 0 = \frac{\partial u_1}{\partial t}.$$

Hence

$$\rho_1 = mN_1 e^{-h \frac{mu_1^2}{2} - eh\chi}$$

and

$$\rho_1 u_1 = B_1,$$

where N_1 and B_1 are constants.

Similarly for the negative atoms we have

$$\rho_2 = mN e^{-h \frac{mu_2^2}{2} + eh\chi},$$

$$\rho_2 u_2 = B_2.$$

Hence the electrical density at a point is

$$\frac{e}{m}(\rho_1 - \rho_2),$$

and the electrical current is

$$= \frac{e}{m}(\rho_1 u_1 - \rho_2 u_2) = \frac{e}{m}(B_1 - B_2) = \gamma \text{ say.}$$

If the group velocities are small compared with v_0 the velocity of light the potential is given by

$$K \frac{\partial^2 \chi}{\partial x^2} = -4\pi \frac{e}{m} (\rho_1 - \rho_2).$$

Now u_1 and u_2 may be small compared with $\frac{1}{\sqrt{hm}}$, *i. e.* small compared with the velocity of sound, and still give large currents.

If this is so we have approximately

$$\rho_1 = mN_1 \epsilon^{-ehx} \left\{ 1 - \frac{hm}{2} \frac{B_1^2}{N_1^2 m^2} \epsilon^{2ehx} \right\},$$

$$\rho_2 = mN_2 \epsilon^{ehx} \left\{ 1 - \frac{hm}{2} \frac{B_2^2}{N_2^2 m^2} \epsilon^{-2ehx} \right\}.$$

Thus, taking K as 1,

$$\frac{\partial^2 \chi}{\partial x^2} = 4\pi e \left\{ \left(N_2 + \frac{h}{2m} \frac{B_1^2}{N_1} \right) \epsilon^{+ehx} - \left(N_1 + \frac{h}{2m} \frac{B_2^2}{N_2} \right) \epsilon^{-ehx} \right\},$$

which is an equation of the same form as before.

The solution is thus

$$\cosh \frac{eh\chi + \alpha}{2} = \frac{1}{\operatorname{sn}(\lambda x + \beta, k)}$$

where

$$\epsilon^{2\alpha} = \frac{N_2 + \frac{h}{2m} \frac{B_1^2}{N_1}}{N_1 + \frac{h}{2m} \frac{B_2^2}{N_2}},$$

$$\lambda^2 = 8\pi h e^2 \sqrt{N_1 N_2 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right) \left(1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right)},$$

$$k^2 = \frac{2 + \frac{B}{\sqrt{N_1 N_2 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right) \left(1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right)}}}{4}.$$

The particular form of solution adopted depends on the values of the arbitrary constants introduced. When there is no potential and no current we have $N_2 = N_1$. Again, if we assert the condition that the total number of atoms, viz. $(N_2 + N_1 + 2N_0) \times (\text{vol.})$ is constant, we may regard N_2 , N_1 , and N_0 as known.

Since the current is made up of two streams we cannot

determine B_1 and B_2 uniquely unless we impose some relation between B_1 and B_2 . The most likely seems $B_1 = -B_2$. If the potential is given at two points then β and B are determined.

For the general discussion of the solution we may then take the form

$$\cosh \frac{eh\chi + \alpha}{2} = \operatorname{sn}(\lambda x + \beta, k),$$

where $\alpha, \lambda, \beta, k$ are supposed known. We get

$$\cosh eh\chi + \alpha = 2 \operatorname{sn}^2(\lambda x + \beta, k) - 1.$$

Now $\cosh eh\chi + \alpha$ is proportional to the matter density of free atoms. Further the density of the molecules is a function of $\left(\frac{\partial\chi}{\partial x}\right)^2$, and the first integral is

$$\begin{aligned} \left(\frac{\partial\chi}{\partial x}\right)^2 &= \frac{8\pi}{h} \sqrt{N_1 N_2 \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right\} \left\{ 1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right\}} \\ &\times \left\{ 2 \cosh eh\chi + \alpha - \frac{B}{\sqrt{N_1 N_2 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right) \left(1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right)}} \right\}. \end{aligned}$$

Thus in general the matter density of the gas is periodic. The distance between points of equal density is given by d where

$$\lambda d = m\omega + m'\omega',$$

where ω and ω' are the complete periods of the elliptic functions and m and m' are the least integers which make d real.

$\operatorname{Sinh} eh\chi + \alpha$, which is proportional to the electrical density, is also periodic in the same period. Where the function $\sinh eh\chi + \alpha$ vanishes we have an equal number of free positive and negative atoms. At such a place there is most chance of recombination. It is probable that such recombination gives rise to luminosity. If the points of maximum matter density coincide with the points of least electrical density, then the above calculation would indicate that we should have very well defined planes of maximum luminosity.

The planes of minimum electrical and maximum matter density will not, however, in general coincide. Thus, though we should still have planes of maximum luminosity, they will not be so well defined.

These considerations suggest that we have something very closely related to the condition of things in a striated vacuum-tube.

In order to test this further, let us consider how the distance between these maxima planes varies as the constant B varies.

Suppose $N_1 = N_2$, and $B_1 = -B_2$,
so that the current

$$\gamma = \frac{2e}{m} B_1.$$

Our first integral takes the form

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h} N_1 \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\} \left\{ 2 \cosh eh\chi - \frac{B}{\left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right) N_1} \right\}.$$

The least value which $\cosh eh\chi$ can have is 1.

Suppose F the value of $\frac{\partial \chi}{\partial x}$ where $\chi = 0$.

$$\frac{-B}{1 + \left(\frac{h}{2m} \frac{B_1^2}{N_1^2}\right) N_1} = \frac{hF^2}{8\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)} - 2,$$

so that

$$2 + \frac{B}{N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)} = 4 - \frac{hF^2}{8\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)}.$$

When $F = 0$ the appropriate solution is

$$\cosh \frac{eh\chi}{2} = \coth \lambda x + \beta$$

where

$$\lambda^2 = 8\pi h e^2 N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right).$$

Here the distance d is infinite.

As F^2 increases from 0 to $\frac{32\pi N_1}{h} \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\}$

the proper form is

$$\cosh \frac{eh\chi}{2} = \frac{1}{\operatorname{sn}(\lambda x + \beta, k)},$$

where

$$\lambda^2 = 8\pi h e^2 N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right),$$

$$\frac{4 - \frac{hF^2}{8\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)}}{4} = 1 - \frac{hF^2}{32\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)};$$

$$k'^2 = \frac{hF^2}{32\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)}$$

For small values of k'

$$d = \frac{1}{\lambda} 2 \log \frac{4}{k'}$$

when $F^2 = \frac{32\pi N_1}{h} \left\{1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right\}$

$$\cosh \frac{eh\chi}{2} = \frac{1}{\sin \lambda x + \beta} \text{ (ordinary circular functions).}$$

$$\lambda^2 = 8\pi h e^2 N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right),$$

and

$$d = \frac{\pi}{\lambda}. \text{ (This is the least value of } d\text{.)}$$

From

$$F^2 = \frac{32\pi N_1}{h} \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right) \text{ to } \infty$$

we get

$$\cosh \frac{eh\chi}{2} = \frac{1}{k'} \frac{dn\lambda x + \beta, k}{\sin \lambda x + \beta, k}$$

where

$$\lambda^2 = 8\pi h e^2 N_1 \left\{1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right\} k'^2$$

and

$$k^2 = 1 - \frac{32\pi N_1}{h} \frac{\left\{1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right\}}{F^2}$$

$$k'^2 = \frac{32\pi N_1}{h} \frac{\left\{1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right\}}{F^2}$$

and if k' is small,

$$d = \frac{1 \times F}{16\pi N_1 e \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)} 2 \log \frac{4}{k'}$$

Now Goldstein (*Wied. Ann.* xv. p. 277, 1883) finds that d is very nearly inversely proportional to the density, while Mr. R. S. Willoughs (*Cav. Lab.*) finds that above a certain strength of current the distance d diminishes as the current increases. N_1 will be proportional to the density multiplied by some function of F , so that the formula for d will agree

fairly well with these experimental results if F^2 lies between $\frac{32\pi N_1}{h} \left\{ 1 + \frac{h}{2m N_1^2} B_1^2 \right\}$ and ∞ .

The distance between the striæ depends on the diameter of the discharge-tube. It is possible that the solution of the general differential equation for χ would lead to this, but it seems hopeless to attack the equation for two dimensions.

Another interesting deduction from the solution above, which has been verified experimentally since I made the calculation, is that while $\frac{\partial \chi}{\partial x}$ is periodic in the striæ the potential χ is not periodic.

The equation $\cosh \frac{eh\chi + \alpha}{2} = \text{sn}(\lambda x + \beta, k)$ may be transformed into

$$\sin \psi = \mu \text{sn}(v, k)^*,$$

where ψ is a linear function of χ ,
 v " " " " x ,
 μ some constant,
 k some modulus.

Now this equation is just of the same form as that for the motion of a simple pendulum under gravity, ψ being the angle, and v the time, and we know that when the pendulum makes complete revolutions it is possible to express ψ as equal to μv and a series of periodic terms.

Thus, χ in general is a linear function of x and a series of periodic terms.

χ must be real, and the series convergent. This will depend on the particular circumstances. That the series must converge to zero in one case is obvious, for if there are no free atoms $\chi = Ax + B$ is a complete solution of the equation.

Further, $\frac{\partial \chi}{\partial x}$ is periodic, although χ is not so.

I understand that from measurements of χ in the striæ, χ is just of the nature we have found, while Mr. H. A. Wilson, at the Cavendish Laboratory, finds that $\frac{\partial \chi}{\partial x}$ is periodic.

* In the equation $\frac{\partial^2 \chi}{\partial x^2} = 8\pi e \sqrt{N_1 N_2} \sinh(eh\chi + \alpha)$ put

$$\begin{aligned} eh\chi + \alpha &= i\psi, \\ x &= it; \end{aligned}$$

and we get

$$\frac{\partial^2 \psi}{\partial t^2} = -8\pi e^2 h \sqrt{N_1 N_2} \sin \psi,$$

which is the equation of motion of a simple pendulum.