Physics. "*On the Separation of Gas Mixtures by Diffusion in a Flowing Gas*". By Dr. G. HERTZ. (Communicated by Prof. P. EHRENFEST.)

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As is well known, the differential equation: $\Delta\rho = 0$, in which ρ represents the density of the diffusing gas, is valid for stationary phenomena of diffusion in media at rest. This equation does not contain the constant of diffusion of the diffusing gas at all. If, therefore, the diffusion of a gas mixture is considered, the ratio of the partial pressures of the components of the mixture is constant throughout the space, i.e. unmixing does not occur with such a stationary diffusion phenomenon. This however, is different, as will be shown in what follows, with stationary phenomena of diffusion in a moving medium. As such a moving medium we take a flowing gas. Let the velocity of this gas medium be $\mathfrak{v}$, and let it satisfy the condition $div\ \mathfrak{v} = 0$. The constant of diffusion of the diffusing gas under definite circumstances be δ, its density ρ, which for the calculation we shall assume to be small compared with the density of the gas medium. The quantity of the diffusing gas passing through the unit surface in the unit of time hence its current density, is equal to the sum of the diffusion and the convection current; it is:

$$\mathfrak{i} = -\delta\, grad\ \rho + \rho\, \mathfrak{v}$$

For stationary phenomena $div\ \mathfrak{i} = 0$, so that taking into account that $div\ \mathfrak{v} = 0$, we get the following differential equation for such phenomena:

$$\Delta\rho = \frac{1}{\delta}(\mathfrak{v},\ grad\ \rho)$$

In contrast with the equation $\Delta\rho = 0$ holding for a medium at rest, this equation contains the constant of diffusion δ. Accordingly the distribution of the density in space is here dependent upon the constant of diffusion. If, therefore, a gas mixture is made to diffuse in a stationary medium the ratio of the partial pressures is constant. On the other hand this ratio is variable in a moving medium; and this brings about the possibility to use this phenomenon for the separation of gas mixtures.

In what follows two special cases will be treated, which it has been possible to realize experimentally, and which can be used for the separation of gas mixtures. In both cases a gas medium flowing with a constant velocity v is used, the direction of which will be chosen as direction of the negative x-axis. For this case the differential equation is:

$$\Delta \varrho = -\frac{v}{\delta}\frac{\partial \varrho}{\partial x}$$ [1])

When we assume $\varrho = \varrho_0$ for $x = 0$, and $\varrho = 0$ for $x = \infty$, we get as a first example the case of diffusion *against* the gas current. The solution is easily seen to be:

$$\varrho = \varrho_0 e^{-\frac{vx}{\delta}}$$

The density of the gas diffusing against the current decreases, therefore, according to an exponential function, the gradient of which depends on the ratio of the current velocity to the diffusion constant. When now a mixture of two gases whose partial pressures for $x = 0$ are ϱ_0 resp. ϱ'_0 diffuses against the current, the following equation is found for the ratio of their partial pressures as function of the place:

$$\frac{\varrho}{\varrho'} = \frac{\varrho_0}{\varrho'_0} e^{-vx\left(\frac{1}{\delta}-\frac{1}{\delta'}\right)}$$

This distribution agrees in form with the distribution of the partial pressures in the field of gravitation determined by the barometer formula, with the exception only that here the quantity $\frac{v}{\delta}$ takes the place of the specific gravity, and the whole pressure gradient can be brought about at a distance of the order of a millimeter.

If this phenomenon is to be used for the separation of a mixture, the gas present at a certain place, e.g. at $x = l$, must be pumped off. The limiting conditions then become $\varrho = \varrho_0$ for $x = 0$ and $\varrho = 0$ for $x = l$. The solution then becomes:

$$\varrho = C\left(e^{-\frac{vx}{\delta}} - e^{-\frac{vl}{\delta}}\right)$$

in which C is a constant. If, as in practice, $e^{-\frac{vl}{\delta}}$ is small compared with 1, C is approximatiely equal to ϱ_0. We thus find for the

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[1]) Compare S. HOLST WEBER, Handelingen van het 17e Nederlandsch Natuur- en Geneeskundig Congres, Leiden 1919.

current density of the diffusing gas, i.e. the quantity which diffuses per unit of time through the unit of crosssection against the current:

$$i = v\,\varrho_0\, e^{-\frac{vl}{\delta}}$$

If a mixture of two gases which at $x = 0$ have the densities ϱ_0 and ϱ'_0 diffuses, the ratio of the quantities of the two gases which diffuse per unit of time against the current is equal to:

$$\frac{i}{i'} = \frac{\varrho_0}{\varrho'_0} e^{-vl\left(\frac{1}{\delta}-\frac{1}{\delta'}\right)}$$

This quantity represents, therefore, the degree of unmixing reached in such a diffusion process; inversely the product vl is determined by the diffusion constants of the gases that are to be separated, and by the degree of unmixing required. In order to make the efficiency also as large as possible, v should be chosen as large as possible and in accordance with this l small, as follows from the equation of the current density.

The second case, which in practice has been realized, is the following one: let again v be the constant velocity of the flowing gas, and let the direction of the current be that of the negative x-axis. At a certain point in this current we now admit the other gas. This gas will then be carried along with the current, and at the same time be scattered to all sides by diffusion. In this case the distribution of the diffusing gas is found by integration of the differential equation:

$$\Delta\varrho = -\frac{v}{\delta}\frac{\partial\varrho}{\partial x}$$

with the limiting condition that at infinity the density of the diffusing gas must be zero. When the point where the gas enters the current, is chosen as origin of the system of coordinates, and the radius vector is called r, we find the solution:

$$\varrho = \frac{C}{r} e^{-\frac{v}{\delta}\frac{r+x}{2}}$$

in which C is a constant. The factor $\frac{C}{r}$ represents diffusion in the medium at rest, the exponential function which is due to the current, is of the same nature as in the first case; only instead of x, we have here $\frac{r+x}{2}$. If, therefore, a gas mixture is introduced into the current, unmixing takes place in this case as well. Further

the same remarks are valid here as in the first case; thus it is also practical here to choose the current velocity great and geometrical dimensions small to render the quantity attained as great as possible.

All these considerations have completely been confirmed by experiment. In order to effect the separation of gas mixtures by diffusion in a flowing gas in practice, it is first of all required that as a medium a gas be chosen that can be easily separated from the diffusing gases. This can be attained in a simple way by using a vapour as medium gas, which can be condensed after having passed the place where the diffusion is brought about. All the experiments made so far, were carried out with water vapour of 15 to 60 cm. pressure. The use of mercury vapour of lower pressure may, possibly, be still more efficient; this will be further investigated.

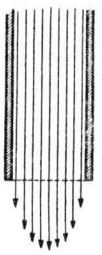

Fig. 1.

The chief point in the construction of apparatus for carrying out the process described above, is the production of a constant vapour current. When a gas passes over a sufficient distance through a cylindrical tube, a current is obtained with parallel stream lines, but the velocity is not constant; it decreases from the axis towards the walls of the tube, as is represented in fig. 1. It is, however, possible to get a current of constant velocity, though over a short distance only, when the gas passes through a wide tube with a suddenly decreasing diameter or when the gas escapes from a vessel through a small hole in the wall. When in this way the medium gas flows from a vessel A into a vessel B (fig. 2), and when the gas mixture that is to be separated, is admitted to the vessel B, the case of diffusion against the gas current is realized. The velocity of the current can then always be chosen such that only the component of the gas mixture that diffuses more rapidly, diffuses against the current and reaches the vessel A, from which it can be pumped off together with part of the medium gas.

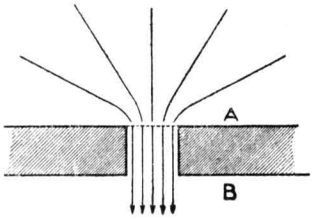

Fig. 2.

This idea was carried out experimentally as follows: the water vapour generated in a vessel heated electrically, flows through S (fig. 3) into a tube closed at the bottom by a metal plate D of a thickness of 1 m.m. This circular plate of a diameter of 28 m.m. has 30 holes of 1 m.m., each, distributed uniformly over its surface. Through these holes the water vapour enters the vessel V, the lower part of which is surrounded by a cooling jacket, so that

the water vapour is condensed. The gas mixture to be separated is admitted through the tube G. A part of this mixture diffuses against the current through the holes in D; this part can be pumped off with part of the water vapour through the tube H. The temperature of the water in the cooling jacket must be regulated in such a way, that the sum of the partial pressure of the water vapour and the pressure of the gas mixture in the vessel V is exactly so much smaller than the pressure of the water vapour admitted through the tube, that the required current velocity is obtained. The appliances used to attain this regulation, will be discussed later. The method described has so far been chiefly used to separate helium-neon mixtures, and has proved very satisfactory. Even, when the process of diffusion was executed only once, from such a mixture containing 30 % helium, helium could be obtained, the purity of which was so great, that in a Geissler-tube at a pressure of 1 m.m. the neon-lines were not visible with an ordiuary spectros cope. Considering the exceedingly great spectral sensitiveness of Helium with regard to very small quantities of Neon, this shows already a very great degree of purity.

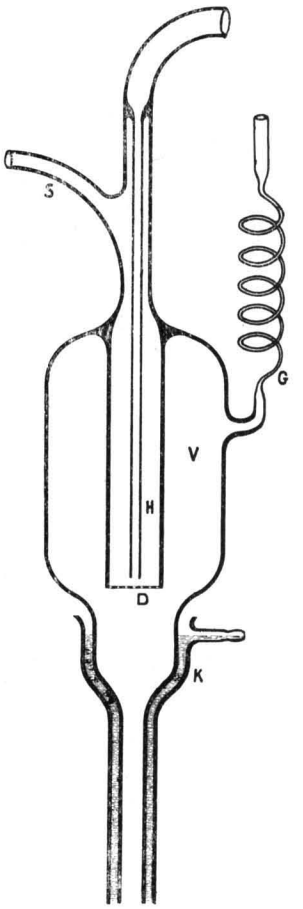

Fig. 3.

Though the unmixing of the gas mixture by diffusion against the gas current was actually as great as was to be expected according to theory, the quantities obtained remained below expectation. This may be explained by considering, that in the method described only part of the cross section of the vapour current is used, because the gas must diffuse from the outside into the jets that issue separately from each hole. In order to deal with greater quantities another apparatus appeared to be more suitable, working according to the second example discussed above. This second case is in so far much more easily realized, as it is not necessary here to keep the current velocity accurately constant. It is immediately seen that with a current as represented in fig. 1, also unmixing of a mixture is to be expected, when this mixture is introduced at a point in the axis of symmetry of the current. The principal part of the

apparatus is reproduced in fig. 4. The water vapour enters through the tube R, which is ground off at the end, so that the water vapour leaves the tube in a cylindrical jet. The gas mixture enters through the tube G, ending in a capillary concentric with R, the end of which is in a plane with the endplane of R. Opposite the tube R at a distance of 3 mm. there is a tube D, the opening of which is formed by a circular sharp edge of a diameter of 6 mm., and manufactured from metal for the purpose. The outer part of the cylindrical jet coming from R is as it were peeled off by the sharp edge. With a suitable choice of the current velocity this outer part of the vapour current practically contains only the component of the mixture which diffuses more rapidly; this component is separated from the water vapour by condensation, and collected in a vessel. By far the greater part of the gas mixture admitted through G passes on through the tube M with the inner part of the vapour current, is also freed of the water vapour by condensation, and again admitted through G by means of a circulation pump.

Fig. 4.

If the apparatus is to work well it is chiefly necessary that the velocity of the current is accurately regulated, and besides it is practical to lead the condensed water vapour back; else the water in the heating vessel would diminish too rapidly. Fig. 5 represents the whole apparatus. In the glass vessel W, which is 50 cm. long and has a diameter of 10 cm. the water is heated electrically by means of a heating wire wound on a layer of asbestos. The pressure of the water vapour in this space can be determined by means of a thermometer T suspended in the vapour. This water-vapour flows through a tube to a bulb B, and from there to the tube R of the diffusion apparatus, while simultaneously the gas mixture to be separated, enters the tube G through a very narrow capillary tube. By the regulation of the pressure of the gas mixture before it enters the capillary tube, an accurate control of the velocity with which the mixture is admitted, is made possible. The two parts, into which the gas current is split up by D, pass on through the tubes H M resp. and reach the condensation vessels C_1 and C_2, which are provided with cooling jackets K_1 and K_2. Here the water vapour is condensed, and the water runs back, to W as is seen in the figure. The part separated by diffusion is collected in C_1, and the rest of the gas mixtures in C_2. Both

these parts tog ether with some water-vapour leave the apparatus each through a very narrow capillary. The water vapour is removed by freezing it out. The separated part is received in a vessel, the rest of the gas mixture, however, is again led back to the apparatus by means of a circulation pump.

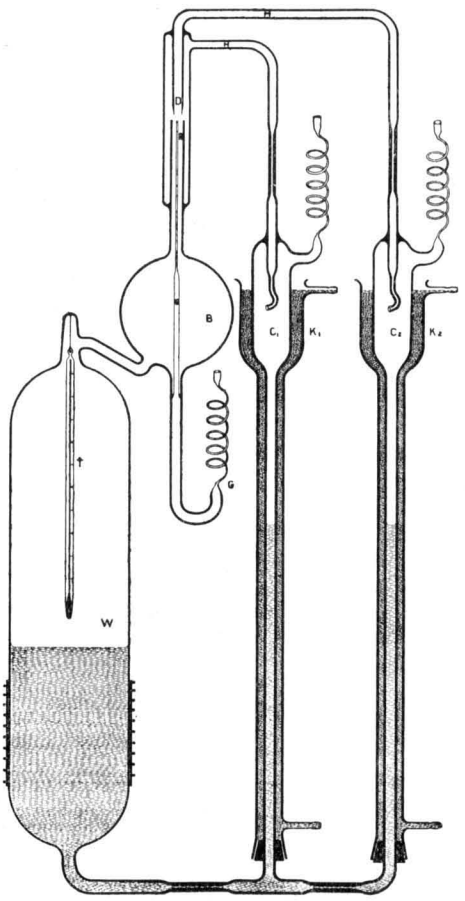

Fig. 5.

The vapour current is controled by regulating the current in the heating spiral wound on W, and the temperatures in K_1 and K_2. The latter is effected in such a way that the water flowing through the cooling jackets with accurately constant velocity is beforehand led through a copper tube, surrounded by a heating coil, so that the temperature of the water depends on the current passing through this heating coil. The check on the current velocity is made possible by the capillaries between H and C_1, and between M and C_2, these causing a difference of pressure between W and C_1 resp. C_2 that is in direct ratio to the current velocity in H resp. M. This difference of pressure can be measured by the difference of level between the condensed water in C_1 resp. C_2 and the water in W. Neither the absolute value of the current velocity nor the temperature of the water in K_1 and K_2 need be known; when the level of the water in the two tubes with regard to the level in W is such, that the unmixing of the gas mixture is satisfactory, the heating current need only be regulated so, that this position is maintained.

It is not necessary to keep the temperature, and with it the density of the vapour, accurately constant, for both the current velocity corresponding to a given difference of pressure between the ends of the capillary tube, and the diffusion constants of the diffusing gases are approximately inversely proportional to the density of the

vapour; accordingly the relation $\frac{v}{d}$ characteristic of the diffusion in a flowing gas is not affected by small fluctuations in the vapour density. In order to prevent condensation of the water vapour against the walls, the whole apparatus is enclosed in a box, in which the air is heated a few degrees above the temperature in W.

The same degree of the separation is obtained by the first and the second method. As regards the quantity obtained the second method however, is considerably better. Only when it is required to separate small quantities, the former method is preferable, as in the second method a certain minimum quantity is required for the circulation.

It is of importance to consider whether our method of the diffusion in a gas current is more efficient with regard to the separation of isotopes than the methods used up to now. This new method is no doubt superior to the usual way of separation by diffusion. It is, however, possible, that when we apply this method to gases with diffusion-constants differing as little as they do for isotopes, small irregularities in the current may have much greater disturbing influence than in neon-helium mixtures. Nor can it, of course, be expected that a mixture of isotopes should be completely separated by a single process of diffusion, for such a process, supposing it be possible in principle, would require a very long time, as can be calculated from the above given formulae. On the other hand, e.g. in neon, a change in the ratio of mixing of the isotopes of about 30 % could be expected as the result of one process of diffusion, so that it might be expected that a fairly far advanced separation can be obtained after not too many repetitions. It is not our intention to use the apparatus described above for the separation of isotopes, as it must undoubtedly be possible to construct apparatus on the same principle, working considerably more rapidly.

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Physical Laboratory of the
"N. V. Philips' Gloeilampenfabrieken."
(Philips' Incandescent Lamp Works).