# Concerning the Effect of Gravity on the Concentration of a Solute.—By Harold S. Davis, B. A., Dalhousie College, Halifax, N. S.*

Read 31st. May, 1911.

Suppose that a solution of uniform concentration is placed in a tube of constant cross-section and of vertical height, $l$, and is exposed to the influence of gravity.

In general the concentration must now change throughout the solution in order to produce equilibrium which obtains after an infinite time.

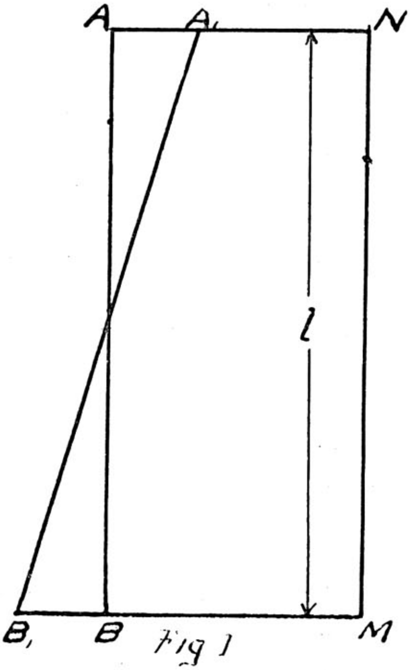

Fig 1

If (Fig. 1) the height of the tube is represented by M N, and the concentration at any point by a distance $x$ perpendicular to M. N, then $x$ will trace out a line A B representing the concentration of the solution at any point. At the beginning, A B will be a straight line parallel to $x\,y$. At final equilibrium it will be a straight line which is in general inclined to M N. See L. Vegard, Contributions to the Theory of Solutions, *Phil. Mag.*, series 6, no. 77, page 258). For any time $t$ less than infinity, A B will represent the distribution of the solute.

---

[*] Published in this part by permission of the council of the N. S. Institute of Science.

In the article referred to above, Vegard proves from considerations of dynamical and thermodynamical equilibrium, that the final distribution of the solute will depend on whether the density of the solution at that particular concentration increases or decreases for an infinitely small increase in concentration. In the special case in which a small change in concentration makes no corresponding change in density, the concentration of the solution will remain uniform throughout even when exposed to gravity.

Suppose now the homogeneous solution is exposed to gravity, its concentration will begin to change, solute flowing from the top to the bottom or vice versa, according as the density at that particular concentration increases or decreases with the concentration. This flow will be comparatively large at first, but will fall away to zero as an exponential function of the time. When equilibrium is reached, there is the same concentration gradient at every height of the column. If now we consider the force of gravity removed, the solution will begin to diffuse back to its initial condition of uniform concentration, and it seems reasonable to suppose that the flow will be exactly similar to that in the original solution, that is it will be comparatively large at first, and will fall away as an exponential function of the time.

If this be true, then the original diffusion flow is exactly similar to one in a tube not exposed to any force such as gravity and where the initial concentration gradient is equal to that which actually exists in final equilibrium in the solution exposed to gravity.

Now it is always assumed that the diffusion of a solute is analagous to the flow of heat, and obeys Fourier's linear diffusion law, and the conditions in the differential equation:

$$D\frac{d^2c}{dx^2} = \frac{dc}{dt}$$

Where $T =$ time.

$c =$ concentration of solute,

$x =$ distance from any fixed plane perpendicular to the direction of flow.

$D =$ a constant for that particular solvent and solute.

Assuming this, the other condition we have is that no solute passes through the limiting layers A N or B M (Fig. 1).

To get this problem into a form suitable for mathematical analysis let us imagine that we have an infinite number of tubes of solution such as in (Fig. 1) of length $l$, and with a concentration gradient as in final equilibrium. Suppose now we place these together end to end so that the end of greatest concentration in one meets the end of greatest concentration in the other (Fig. 2).

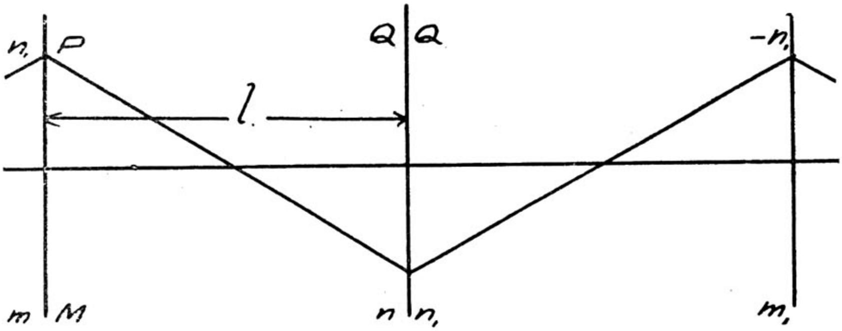

FIG. 2

Diffusion begins and the solute in the tube M N flows in the direction of the gradient and similarly in the other tubes. The concentration at the plane M P therefore decreases and that at $n$ Q increases. *But since there is no gradient at the plane P M or at the plane n Q, so solute can pass through them,* which is the condition required in our problem.

Now, since the concentration in M $n$ obeys Fourier's linear diffusion law, it is a function of the distance $x$ from the plane P M, and of the time T, and may be expanded in a Fourier's series, but since $\Phi\ (x) = \Phi\ (-x)$ only cosine terms enter.

Let $$\Phi(x) = \left(A_o \times A_1 \operatorname{Cos} \frac{\pi}{l} x + A_2 \operatorname{Cos} \frac{2\pi}{l} x + \ldots\ldots\ldots\ldots\right)$$

$$\text{where } A_m = \frac{1}{l}\int_o^{2l} \Phi(x) \operatorname{Cos} \frac{m\pi}{l} dx$$

$$\text{where } A_o = \frac{1}{2l}\int_o^{2l} \Phi(x)\, dx.$$

Let ($a$) be the difference in concentration between the initial and final at the plane PM, which is of course equal to that at the plane NQ

Then at time $T = o$

$$\Phi(x) = a - \frac{2ax}{l} \text{ from } o \text{ to } l$$

$$\Phi(x) = \frac{2ax}{l} - 3a \text{ from } l \text{ to } 2l$$

$$\therefore A_m = \frac{1}{l}\int_o^l \left(a - \frac{2ax}{l}\right) \operatorname{Cos} \frac{m\pi}{l} x\, dx$$

$$+ \frac{1}{l}\int_l^{2l} \left(\frac{2ax}{l} - 3a\right) \operatorname{Cos} \frac{m\pi}{l} x\, dx$$

$$\therefore A_m = \left[\frac{al}{m\pi l} \operatorname{Sin} \frac{m\pi x}{l}\right]_o^l - \frac{2a}{ll}\left[\frac{xl}{m\pi} \operatorname{Sin} \frac{m\pi}{l} x + \frac{l^2}{m^2\pi^2} \operatorname{Cos} \frac{m\pi x}{l}\right]_o^l$$

$$+ \frac{}{l}\frac{2a}{l}\left[\frac{xl}{m\pi} \operatorname{Sin} \frac{m\pi}{l} x + \frac{l^2}{m^2\pi^2} \operatorname{Cos} \frac{m\pi}{l} x \right]_l^{2l}$$

$$- \left[\frac{3a}{l} \frac{l}{m\pi} \operatorname{Sin} \frac{m\pi}{l} x \right]_o^{2l}$$

$$\therefore Am = \left( \ .\ \ .\ \ .\ \ .\ \left(\operatorname{Sin} m\pi\right)\right.$$

$$\left. + \frac{2a}{m^2\pi^2}\left( - \operatorname{Cos} m\pi + \operatorname{Cos} o + \operatorname{Cos} 2m\pi - \operatorname{Cos} m\pi\right)\right)$$

$$= o \text{ when } \underline{\text{“}m\text{”}} \text{ is even}$$

$$= \frac{8a}{m^2\pi^2} \text{ when } \underline{\text{“}m\text{”}} \text{ is odd}$$

In the same way ;

$$A_o = \frac{1}{2l}\int_o^l \left(a - \frac{2ax}{l}\right) dx + \frac{1}{2l}\int^{2l} \left(\frac{2ax}{l} - 3a\right) dx$$

$$= \frac{1}{2l}\left[al - al + 4al - 6al - al + 3al\right] = o$$

So. If $\Phi\ (x) = \frac{8a}{\pi^2}\left(\text{Cos}\ \frac{\pi}{l}\ x + \frac{1}{9}\text{Cos}\ \frac{3\pi}{l}\ x + \frac{1}{2l}\ \text{Cos}\ \frac{5\pi}{l}\ x\right.$

$\left. + \ldots\ldots\ldots\ldots\ \ldots\ldots\ \text{etc}\right)$

and if $x = l$ then $\Phi\ (x) = -a$

$x = o$ then $\Phi\ (x) = a$

$x = \frac{l}{2}$ then $\Phi\ (x) = o$

which shows that the analysis is correct physically. So that at any time, T

$$\Phi\ (x) = \frac{8a}{\pi^2}\left(\epsilon^{\frac{-\pi^2 DT}{l^2}}\ \text{Cos}\ \frac{\pi x}{l} + \frac{1}{9}\epsilon^{\frac{-9\pi^2 DT}{l^2}}\ \text{Cos}\ \frac{3\pi}{l}\ x\right.$$

$$\left. + \frac{1}{25}\epsilon^{\frac{-25\pi^2 DT}{l}}\ \text{Cos}\ \frac{5\pi}{l}\ x \ldots\ldots\ldots\ldots\right)$$

which is a Fourier's Series as is readily seen.

If then we have ($D$) the diffusion coefficient of the substance and ($l$) the length of the solution tube, and ($a$) the initial difference in concentration at the limiting layer from that at final equilibrium, we can calculate what will be the value of ($a$) at any future time.

Three things are necessary that this change in concentration, due to gravity, may be detected in a solution in a reasonable time:

(1) The change in density with concentration must be large at that concentration.

(2) The diffusion constant must be as large as possible.

(3) The substance must lend itself readily to the detection of change in concentration.

It seems likely that some organic solutes and solvents can be found which will have all these factors at a maximum. Data on the first two factors can be found for some substances in Landolt Börnstein's tables, and of these cane sugar seems to be one of the most satisfactory. It has a large diffusion constant, and can be obtained very pure, and its concentration can be accurately estimated by the polariscope.

The following calculations are made for a tube 3 meters in length, and D for cane sugar is taken as .300 as about the mean of the results of Grahm and Arrhenius.

D = .300 where the cm. is the unit of length, the gram the unit of mass, and the day the unit of time.

Calculation of the fall for one year; that is, for $a$ at x = 0, and t = 365.

$$a^t = \frac{8a}{\pi^2}\left( \epsilon^{\frac{-10 \times .3 \times 365}{90000 \times 1}} + \frac{1}{9}\epsilon^{\frac{-9 \times 10 \times 0.3 \times 365}{90000 \times 1}} \quad \ldots\ldots\ldots \right)$$

$$= \frac{8a}{\pi^2}\left( \epsilon^{-0.012} + \frac{1}{9}\epsilon^{-0.108} \quad \ldots\ldots\ldots\ldots\ldots\ldots \right)$$

$$= \frac{8a}{\pi^2}\left( 0.988. + 0.098 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \right)$$

$= o.9a$ approximately.

So that in a tube of this length the fall in concentration of the sugar solution at the end of one year would only be about one-tenth of the total fall after an infinite time. For a concentration of 1 to 4 this would be about ten per cent. of $10 \times 10^{-7} \times 150 = 15 \times 10^{-6}$ gr. which is a change of concentration that in a solution of that strength would defy detection.

Nor would any material advantage be obtained by either shortening or lengthening the tube, for in the first case the total effect is decreased and soon gets beyond the limit of detection, and in the other, the time to obtain the same percentage fall is increased so as to soon debar experimental verification.

This effect would then be difficult to show in the laboratory, except perhaps for some organic substances, and for these there is no available data on diffusion constants or on density. In nature, however, there are immense bodies of water in the ocaen. These have been there for a long time, though with disturbing factors, and here this effect might be detected.

Practically the only comprehensive and reliable data on the composition of sea water is to be found in the *Reports of H. M. S. Challenger,* Physics and Chemistry, vol. 1. A great number of samples of waters from various latitudes and depths were secured and analysed. The whole results are given. There is also an excellent report on deep-sea temperatures.

Now it will be well to consider whether there are other factors present which would modify the effect in question. These are:

(1) Ocean currents which tend by continually stirring up the water to keep the whole at constant concentration.

(2) The effect of hydrostatic pressure. In the article referred to above, Vegard assumes that the fluid is incompressible and his results are worked out on that assumption. (See also Ostwald, *Solutions,* Muir's translation, 1894, p. 61).

(3) Temperature.

The effect of temperature on the concentration of a solute is difficult to calculate for this reason.

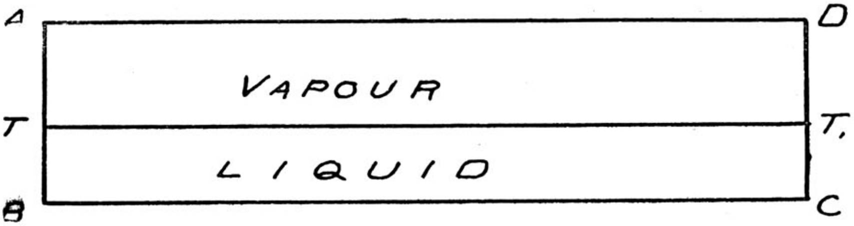

FIG. 3.

Suppose we have the space A, B, C. D (Fig. 3) filled with a liquid and its vapour, and attempt to form a temperature gradient between A, B and D, C. Then, if we keep the planes A, B and C, D at two fixed and different temperatures, the same amount of heat will not pass out through the one at lower temperature as passes in through the one at higher temperature for two reasons:

(1) The liquid itself will circulate and do work because every liquid changes its specific volume with temperature, consequently if it expands with heat, the heated part will rise to the top and give place to cooler and *vice versa* if it contracts.

(2) The vapour will circulate from points of higher vapour pressure to those of lower.

It would then be impossible to obtain a permanent fixed horizontal temperature gradient in a liquid. Perhaps this fact has some bearing on ocean currents and trade-winds, since the tendency is for the water at the poles to be colder than that at the equator. Currents of water and water vapour must result.

The only possible permanent temperature gradient, then, which can exist in a liquid, that changes its specific volume with temperature, is a vertical one. The direction of this gradient will be from top to bottom or *vice versa* according as the liquid expands or contracts with heat.

Suppose such a gradient to exist in a solvent, and let solute be introduced without disturbing the solvent till it is saturated at each point. Then if we neglect the change in specific gravity due to the introduction of solute or suppose it to be less than that due to the temperature gradient, there will be an increase or decrease in the concentration with height, in the case of a temperature gradient from top to bottom, according as the solubility increases or decreases with temperature.

If such a concentration gradient exists for the saturated solution, there would still exist one, thought not the same in magnitude in solutions not saturated.

Taking the case where increase of temperature is followed by increase of solubility as is the case of most salts in sea water, and where the direction of the temperature gradient and of the flow of heat is downward, as in the ocean, the concentration will increase from the bottom upward.

Now the temperature of the ocean decreases fairly rapidly down to about 800 fathoms, from about 70 F. to 38 F., but after that for the next 1,000 fathoms or more it decreases only 1 to 2 F, so that the temperature of the ocean at great depths is remarkably constant. See *Challenger Reports,* vol. 1, table 6, and also the report on deep-sea temperatures).

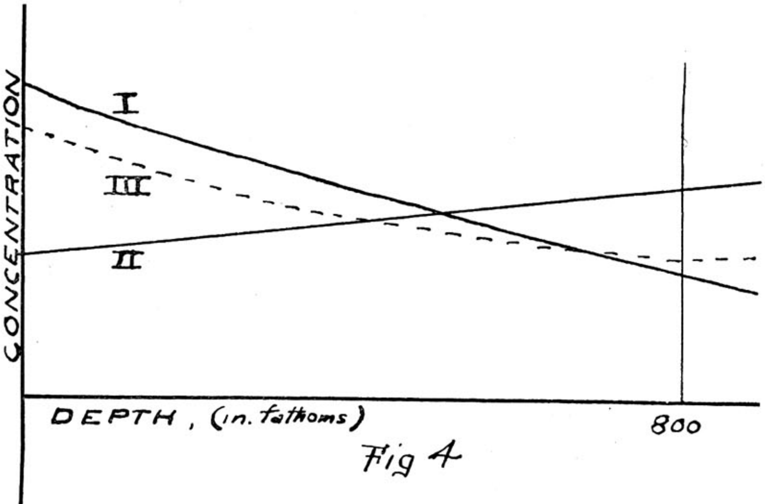

Fig 4

The effect of temperature will thus be a decrease in concentration with depth down to the point where the temperature becomes fairly constant. After this the effect of temperature will gradually die away.

Superposed on this is the effect of gravity, which, as we have seen, will, for inorganic salts, be to increase the concentration with the depth. I have roughly represented the first effect by the curve (1), Fig. 4, and that of the second by curve (2). They will give a resultant curve (3) of change in concentration with depth, and if we suppose the first effect to be the greater near the surface, then the concentration will first decrease, not necessarily uniformly, down to a certain point where the two effects just counterbalance, and from thence will increase steadily to the bottom.

This would account for the actual distribution of the saline contents of sea water as actually found from the summary of the researches on the "Challenger" as given by Dittmar. (See *Encyclopædia Britannica,* 9th edit., "Sea Water").

"In places where there is active dilution at the surface, the salinity as a rule increases down to some 50 or 100 fathoms, but thence downward it follows the general rule, *that is, it decreases down to 800 or 1,000 fathoms, and thence increases steadily to the bottom.*"

Of the data available from the reports on the concentration of the separate constituents, only that of the absorbed gases is of value since the others were determined relatively to the total chlorine content.

Apart from the fact of the large increase of solubility of gases with temperature, the increase of density with concentration, though positive, is extremely small and difficult to measure. (S e Ostwald, Solutions, p. 32).

It was found that:

(1) The amount of nitrogen increases with the depth.

(2) The amount of oxygen decreases with the depth.

But as a matter of fact, the increase of density with concentration for oxygen is greater than for nitrogen, which ought therefore to show a greater increase with the depth.

Dittmar explains the decrease of oxygen as being due to oxidation.

(For the greater part of the mathematics in this paper I am indebted to Dr. H. L. Bronson, of the Department of Physics, Dalhousie College.)