question must wait further knowledge either of the number or of the physical properties—especially the specific gravities—of the rare-earth elements.

Summary.

It has been shown in Part I that, in physical calculations, symmetry is often more surely obtained by neglecting atomic weights and substituting specific gravity, valence or position-number in the place of atomic weight; that a harmonic relation, which has not been previously sufficiently recognized, exists between these three properties in any one period. In Part II there has been proposed an arrangement of the periodic system, slightly different from the usual one but in harmony with the fundamental physical property specific gravity, and more rational especially in regard to the heavy metals of the long series.

AMHERST COLLEGE,
AMHERST, MASSACHUSETTS.

THE DIFFUSION OF OXYGEN IN WATER.

BY TOR CARLSON.

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In a previous investigation[1] it was shown from determinations of the rate of solution of carbon dioxide and oxygen in water or the rate of escape of the gases from water that, if one adopts Nernst's theory for the phenomenon of solution, the ratio between the coefficients of diffusion of the gases mentioned may be calculated to be 1.158. For the coefficient of diffusion of carbon dioxide there are available closely concordant values obtained at 16° by two different observers, *viz.*: 1.36 and 1.41 (per sq. cm. per 24 hours) by Stefan,[2] and 1.37 by Hüfner,[3] who used hydrophane plates. For oxygen, moreover, Hüfner (with hydrophane plates and counter-diffusion of nitrogen) found 1.62 at 16°, and Hagenbach,[4] in water containing 20 per cent. gelatin, obtained the value 7.58 at 14°; but in each case only one determination was made. Hagenbach also states that the gelatin offered greater resistance to the diffusing gas molecules than pure water, which in a 20 per cent. gelatin solution was on an average 1.5 times as great. Consequently the coefficient of diffusion for oxygen in water in Hagenbach's experiment amounts to 11.37 (14°) per square centimeter per 24 hours.[5] If the coefficient of carbon dioxide be taken as 1.38 (16°), the mean of the above three determinations, then the ratio between the coefficients of diffusion for oxygen and carbon dioxide

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[1] Tor Carlson, *Meddel. fran Vet. Akad. Nobelinstitut.*, Vol. II, No. 5, 1911.

[2] *Sitzb. Wien Akad.*, 77, Abth. II, 37 (1878).

[3] *Wied. Ann.*, 60, 134 (1897).

[4] *Ibid.*, 65, 673 (1898).

[5] For the carbon dioxide in a 20 per cent. solution of gelatin Hagenbach obtained the numbers 0.843 and 0.770, giving the mean value 1.21, calculated as above for water.

according to Hüfner's experiments would be 1.174, and according to Hagenbach's 8.839 (uncorrected), or in the latter case about 7 times as great as in the former.

It is therefore of special interest to obtain a new determination of the diffusion coefficient of oxygen. As is well known, Wroblewsky[1] was the first to attempt to ascertain the law in accordance with which carbon dioxide diffuses in water. His attempt failed because, when he allowed the gas to enter at the top of a column of water, the upper layers were first saturated with it, and hence became heavier and sank, thus causing currents in the water which disturbed the steady process of diffusion. Soon afterwards,[2] however, Stefan proved that the occurrence of currents (and their disturbing influence) depends on the width of the test-pipe, and that they might be almost entirely prevented if the cross section of the pipe were made small enough, at most 1 millimeter. With such pipes Stefan succeeded in proving the correctness of the assumed law regarding the diffusion of carbon dioxide in water and alcohol, *i. e.*, he proved that Fick's supposition in accordance with which the movements of a salt through its solvent follow analogous rules to those demanded by Fourier's theory of the conduction of heat, is also applicable to the diffusion of dissolved gases in fluids. Stefan's experiments were of two kinds, in one kind, the carbonic acid was made to traverse a column of fluid made as long as possible, and assumed to be infinitly long, while in the other the gas had access to the open air through a short column of water. It is evident, however, that when experimenting with a gas whose coefficient of absorption is relatively small, like that of oxygen in water, Stefan's method is not very suitable. In order to obtain an accurately measurable diminution of the volume of gas in such a case, too long a time would be necessary for the experiment, and even supposing it were possible to keep the temperature constant, considerable disturbances would be inevitable, owing to the evaporation of the fluid.

Agar-agar or gelatin solution may be used for determinations of diffusion (compare Pringsheim,[3] Hoppe-Seyler,[4] and Voigtländer,[5] etc., on diffusion of saline solutions), and by this means currents due to variations of density may be avoided, as was proved by Hagenbach's experiments with gases which are indifferent to gelatin. As regards oxygen, however, the high value of the diffusion coefficient arrived at by Hagenbach[2] is in all probability to be attributed to a process of oxidation in the gelatin, so that the figures given by him represent not only the amount of oxygen which diffused, but also the quantity which was chemically absorbed.

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[1] *Wied. Ann.*, 2, 481 (1877).

[2] *Loc. cit.*

[3] *Z. physik. Chem.*, **17**, 473 (1893).

[4] *Ibid.*, **19**, 411 (1894).

[5] *Ibid.*, **3**, 313 (1889).

At the suggestion of Professor Svante Arrhenius I added potassium chloride (about 1 per cent.) to the diffusion liquid. The reduction in the diffusion of the oxygen caused by this is relatively slight, as proven by Arrhenius'[1] investigations of the rate of diffusion of acetic acid in water and in normal potassium chloride solution (decrease 0.3 per cent.) and by Abegg's[2] on that of ammonia in water and in about normal potassium chloride solution (decrease 0.8 per cent.).

The diffusion experiments which I shall describe were carried out in the following manner. To each of two plane parallel plate-glass slabs, pressed against each other by springs, half a glass tube of even caliber (about 4.5 cm. in diameter) was carefully cemented. The tube fixed in the lower slab was narrowed at the free end, and continued by a three-way cock. The upper tube was finished off by a plane slab of glass in the center of which a capillary tube was inserted. By means of a screw contrivance of small pitch the upper slab could be cautiously pushed along the lower, so that the two glass tubes were made to occupy different positions in relation to one another; and in each slab there was inserted a three-way glass cock. The lower cylinder was filled with as much mercury as was required to make the height of the diffusion fluid the same in both halves of the cylinder.

The quantity of gas passing through a cross section of the cylinder in an infinitesimally short time is proportional to the concentration at the cross section, to this infinitesimal time interval, and to the rate of alteration of the concentration of the gas, at the cross section considered. If the concentration of the gas be represented by r, then $-dr/dx$ is the alteration of the concentration in any section, the position of which is determined by the distance x, measured along the length of the cylinder. The quantity passing through a section q in a certain interval of time is therefore expressed by

$$m = -k.\, q.\, dr/dx.\, dt,$$

where k represents the coefficient of diffusion. Since r is a mass divided by a volume, it will easily be seen from this formula that k signifies a surface divided by a time. If the difference of the quantity of gas which during the time dt passes through the end surface of a small length dx of the cylinder be expressed by $(m + dm/dx.\, dx) - m$, and this be divided by the increase in quantity, which takes place in this small length during the same period we have

$$-dm/dx.\, dx = q.\, dx\, dr/dt.\, dt,$$

whence for r we obtain the differential equation,

$$dr/dt = k.\, d^2r/dx^2.$$

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[1] *Z. physik. Chem.*, 10, 51 (1892).

[2] *Ibid.*, 11, 248 (1893).

The solution of this equation, in cases where it treats of a limited column of fluid, gives r in the form of a periodical series, and from that, by a well known method, one may calculate the amount of gas escaping from the lower half of the tube. Again, if at the time $t = 0$ the distribution of the gas in the liquid is such that one part of the cylinder shows the constant concentration a, while another part has the concentration O, then the mass of gas A, passing through the surface of separation between these two parts, during the time t, is given by the expression[1]

$$A = a.q\sqrt{k.t/\pi}.$$

This formula, strictly speaking, is only applicable in those cases where the two parts of the cylinder are infinitly long, but it may be used for cylinders of finite length, if the time of experiment be so chosen that variations in the condition of the two end strata during this time may be disregarded in comparison with the accuracy attained in the measurement. According to Stefan[2] this formula can invariably be employed for movements of diffusion, provided that the quantity $\pi^2.\ k.\ t > l^2$.

In the experiments in question, $k < 2$, $t < 9$ and $l = 11.2$, so that the limiting value was not reached even in the most unfavorable case.

The diffusion experiments were carried on in the following manner: the upper cylinder, placed immediately above the cock in the lower slab, was filled with air-free distilled water which was allowed to run through it from the bottom upwards for 15 to 20 minutes, afterwards the cock was closed and the capillary tube shut off by a rubber band with a glass stopper inserted into it. At the same time a 1 per cent. potassium chloride solution, in which oxygen, or in other cases carbonic acid gas, had previously been dissolved, was made to run through the lower cylinder by means of a glass tube which opened on the surface of the mercury. When the cylinders had been filled in this manner, the front part of the upper glass slab was pushed above the free portion of the lower cylinder, the whole apparatus being set up (with the cylinders in an exactly vertical position) on a firm base, free from possibility of vibration, in a basement room with double walls of masonry. The variations of temperature in the room during the time the experiments were carried on amounted to only ±0.2° (measured by a self-registering Richards thermometer). When the contents of the cylinders had come to the temperature of the room, the upper cylinder was screwed on to the lower, and the precise time noted.

After a certain number of days the cylinders were pushed past each other till the cock in the upper slab stood exactly above the lower cylinder. In order to prevent the fluid coming in contact with the air, the contents of the cylinders were taken out for analysis by forcing mercury from a

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[1] Stefan, *Sitzb. Wien Akad.*, 79, Abth. II, 177 (1879).

[2] *Loc. cit.*

level-tube into the lower cylinder, where it displaced the diffusion fluid, which then passed to a tube, filled with mercury, of the same capacity as the cylinders, the tube at either end being provided with a three-way Miescher-Geissler cock. During this displacement the mercury ran out of the tube at the same rate as the fluid was forced in. Subsequently the upper cylinder was placed above the surface of the mercury, which was now on a level with the upper surface of the lower slab, and its contents forced out in the same manner.

The quantity of oxygen dissolved was determined by Winkler's[1] method. Through the one cock of the analysis tube 3 cc. of an alkaline potassium iodide solution were introduced, and through the other 3 cc. of a solution of manganese chloride while a corresponding quantity of fluid was allowed to run off. The precipitate was dissolved by means of 5 cc. of concentrated hydrochloric acid forced under it; the solution was washed into a beaker, and titrated with 0.01 *N* thiosulfate and starch.

In the experiments with carbon dioxide, the diffusion fluid was collected in a beaker filled with air free from carbon dioxide, and containing a solution of barium hydroxide and barium chloride. After the solutions had stood for 24 hours, the excess of barium hydroxide was titrated with $^1/_{20}$ *N* hydrochloric acid and phenolphthalein.

The water, boiled in vacuum and run through the upper cylinder, may be considered (excluding experimental errors) to be free from air; by Winkler's method the presence of 0.01–0.02 cc. oxygen per liter of water could be detected.

The following experiments were made at an average temperature of 18.2° (± 0.2). The length (l) of each diffusion cylinder was 11.2 centimeters. In the table t represents the time of diffusion expressed in days; a_I, quantity of diffused oxygen (carbon dioxide respectively) in cubic centimeters per liter, in the diffusion fluid from the upper cylinder when the experiment was interrupted; a_{II}, the corresponding quantity in the fluid of the lower cylinder; k, the constant of diffusion per square cm. per day.

Therefore $a_I = a_I + a_{II}/l \,.\, \sqrt{k.t/\pi}$.

Carbon Dioxide:

	I.	II.	III.	Mean.
t	7	5	9	...
a_I	94.4	92.8	123.7	...
a_{II}	489.4	583.2	532.4	...
k	1.472	1.487	1.466	1.475

Oxygen:

	I.	II.	III.	Mean.
t	6	6	5.9	...
a_I	3.95	15.24	18.28	...
a_{II}	20.58	2.96	3.48	...
k	1.702	1.745	1.713	1.720

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[1] *Ber.*, **22**, 1764 (1889).

If the above coefficients of diffusion be corrected to 16° (corr. 3 per cent. per degree), we get $k_{CO_2} = 1.378$ and $k_{O_2} = 1.607$, and it is evident that they agree fairly well with the values of Stefan and Hüfner (cited above). Hagenbach's figures (11.37 uncorr.) for the diffusion of oxygen in water must therefore be considered quite incorrect, due to the source of error mentioned above. Further, the ratio between the coefficients of oxygen and carbon dioxide, according to the above experiments, is *1.166*, and this result closely approximates to that calculated for the gases in question from the measurement of the rates of escape of the gases from solution.[1]

Finally, the relation of the results may be considered to be the so-called Exner Rule, according to which the rate of diffusion of a gas is inversely proportional to the square root of its density.

That is, $k_{O_2} : k_{CO_2} = \sqrt{1.5202} : \sqrt{1.1056} = 1.173$.

This result closely agrees with the ratio obtained in the above research.

EXPERIMENTALFALTET, SWEDEN,
NOBEL INSTITUTION PHYSICAL CHEMISTRY LABORATORY.

THE FORMATION OF DOUBLE SALTS.

[FOURTH PAPER.]

BY H. W. FOOTE AND P. T. WALDEN.

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In two previous articles from this laboratory[2] the double salts which form from water have been compared with those which form from non aqueous solvents at the same temperature. It was shown that when a double salt crystallizes from water with water of crystallization, the latter in general appears to be an essential constituent of the salt, and the substitution of another solvent may affect the type of double salt produced giving an entirely different ratio between the single salts and between these and the solvent of crystallization. On the other hand, double salts which crystallize from various solvents without combining with them appear always to form the same types. In short, double salts with solvent of crystallization are really triple molecular compounds and have no necessary type relation to the true double salt, which is essentially a dual molecular compound.

It is evident that a double salt may form without solvent of crystallization from certain solvents, giving always the same types, and may combine with others, changing the type of salt. In the present investigation, mixtures of cupric chloride with potassium chloride and with ammonium chloride have been studied. Both systems have been thoroughly investigated previously in water solution and only hydrated double salts ob-

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[1] Tor Carlson, *Meddel. fran Vet. Akad. Nobelinstitut.*, Vol. II, No. 5, 1911.

[2] THIS JOURNAL, **32**, 618 (1910); **33**, 459 (1911).