



VIII. The diffusion of alkali salt vapours in flames

Prof. H.A. Wilson F.R.S. F.R.S.C.

To cite this article: Prof. H.A. Wilson F.R.S. F.R.S.C. (1912) VIII. The diffusion of alkali salt vapours in flames , Philosophical Magazine Series 6, 24:139, 118-125, DOI: [10.1080/14786440708637313](https://doi.org/10.1080/14786440708637313)

To link to this article: <http://dx.doi.org/10.1080/14786440708637313>



Published online: 20 Apr 2009.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)



Citing articles: 4 View citing articles [↗](#)

over which it passes. This introduces factors of which no account is taken in the above investigation.

The velocity of sound in ether at 0° calculated from the above expression is 1787 metres per second, using the value of P_n given by the equation $P_n = L_1 \rho$. The value found by experiment is 1145 metres per sec., which is somewhat smaller than the calculated value. Since V_v , according to equation (9), may be expressed at corresponding states as a multiple of its critical value, a much better agreement with the facts would probably be obtained if we write $V_s = S_1 V_v$, where V_s denotes the velocity of sound and S_1 a quantity which has the same value for all substances at corresponding states. The value S_1 will probably not vary much with the temperature, at a temperature $\frac{T_c}{1.7}$ it is from the foregoing equal to .639.

V_s thus varies with the nature of the liquid in the same way as V_v given by equation (9), which, it should be noticed, holds for matter of any density. If the ether behaved as a perfect gas the velocity of sound would be 302 metres per sec., a very much smaller value than found in practice.

The various formulæ deduced in this paper will be further tested in a paper that will appear in the Proc. of the Camb. Phil. Soc. vol. xvi. part vii.

Cambridge,
March 20, 1912.

VIII. *The Diffusion of Alkali Salt Vapours in Flames.*
By Prof. H. A. WILSON, F.R.S., F.R.S.C.*

THE experiments described in the following paper were undertaken with the object of finding the coefficients of diffusion of alkali salt vapours in a Bunsen flame. The light emitted by flames containing alkali salt vapours appears to be due to atoms of the alkali metal probably electrically neutral † but possibly positively charged. Probably an atom of the metal under the influence of the violent collisions with other atoms loses negative electrons, and so becomes a positive ion. Since, however, many free negative electrons are present in the flame even in the absence of salt, it seems certain that such a positive ion must very soon be neutralized by recombination with electrons. The metal atom therefore will be a

* Communicated by the Author.

† Smithells, Dawson, and Wilson, Phil. Trans. A. vol. exciii. p. 89 (1899).

positive ion for only a fraction of the time. The process of recombination probably sets up vibrations inside the atom which produce radiation, so that the radiation is emitted by the atoms when neutral, or at any rate when with less than their maximum positive charge. The great facility with which the alkali metals lose electrons makes it possible that at the very high temperature of the flame they may lose more than one negative electron. The velocity of the positive ions of salt vapours in flames has been determined by the writer and by others, so that a knowledge of their coefficients of diffusion enables their charge to be calculated by the well-known method first used by Townsend*.

The method I have used to get the coefficients of diffusion is very simple. A small bead of salt on a platinum wire is put in the flame and the shape of the region surrounding the bead which emits light is measured. From this and the velocity of the flame gases the coefficient of diffusion can be easily calculated.

The bead of salt evaporates at a very constant rate, and can be regarded as a constant point source of salt vapour in the stream of flame gases. The vapour from the bead diffuses into the surrounding gas, and its concentration at any point can be easily calculated by the theory of diffusion.

Take the origin at the bead and the axis of x along the direction of motion of the flame gases, and let their velocity be v . Consider a small rectangular parallelepiped with sides ∂x , ∂y , ∂z . with its centre at the point x , y , z . Let c denote the amount of salt vapour per c. c. and K its coefficient of diffusion. The amount of vapour entering a side of the parallelepiped of area $\partial y \partial z$ is

$$\left\{ -K \left(\frac{dc}{dx} - \frac{1}{2} \partial x \frac{d^2c}{dx^2} \right) + v \left(c - \frac{1}{2} \partial x \frac{dc}{dx} \right) \right\} \partial y \partial z;$$

the amount leaving through the opposite side is

$$\left\{ -K \left(\frac{dc}{dx} + \frac{1}{2} \partial x \frac{d^2c}{dx^2} \right) + v \left(c + \frac{1}{2} \partial x \frac{dc}{dx} \right) \right\} \partial y \partial z.$$

Hence the rate of increase of the amount inside for these two sides is

$$\left\{ K \frac{d^2c}{dx^2} - v \frac{dc}{dx} \right\} \partial x \partial y \partial z.$$

* Phil. Trans. A. vol. cxciii. p. 129 (1900).

For the other two pairs of sides the rate of increase is

$$K \left(\frac{d^2c}{dy^2} + \frac{d^2c}{dz^2} \right) \partial x \partial y \partial z.$$

Hence in a steady state we have

$$K \left(\frac{d^2c}{dx^2} + \frac{d^2c}{dy^2} + \frac{d^2c}{dz^2} \right) - v \frac{dc}{dx} = 0. \quad \dots (1)$$

To determine the distribution of the salt vapour round the bead of salt we have to find a solution of this equation satisfying the conditions that at the origin there is a constant source of salt vapour, and that at very great distances from the origin the concentration is very small. Such a solution of (1) is

$$c = \frac{A e^{\alpha(x-r)}}{r}, \quad \dots (2)$$

where $r = \sqrt{x^2 + y^2 + z^2}$, and A and α are constants*.

If this is put in (1) we find that $\alpha = v/2K$. When x and r are very small (2) gives $c = A/r$; so that if q is the amount of salt evaporating per second we have

$$-K \frac{dc}{dr} 4\pi r^2 = 4\pi A K = q;$$

or $A = q/4\pi K$.

Hence $c = \frac{q}{4\pi K r} e^{\frac{v}{2K}(x-r)}$. $\dots (3)$

Owing to the disturbance of the flow of the gases by the bead this equation will not be exactly true close to the bead, but it will hold accurately at distances large compared with the radius of the bead. The shape of the region round the bead which emits visible light will be bounded by a surface over which c has a constant small value, say c' . If therefore we observe the values of x and r at two points on this surface, we have

$$c' = \frac{q}{4\pi K r_1} e^{\frac{v}{2K}(x_1 - r_1)},$$

$$c' = \frac{q}{4\pi K r_2} e^{\frac{v}{2K}(x_2 - r_2)},$$

* H. A. Wilson, Proc. Camb. Phil. Soc. vol. xii. pt. 5 (1904).

which give

$$K = \frac{v(x_2 - x_1 - r_1 + r_2)}{2 \log r_2/r_1}.$$

The shape of the region emitting light is rather like an ellipsoid of revolution with the long axis vertical and the bead at the lower focus. I have found it convenient in practice to observe the greatest horizontal diameter and the corresponding value of r . To find the maximum value of the diameter we differentiate

$$c' = \frac{q}{4\pi K r} \epsilon^{\frac{v}{2K}(x-r)},$$

and put $dy/dx=0$ and $z=0$, which gives

$$K = \frac{v}{2} \frac{r_m}{x_m} (r_m - x_m),$$

where r_m and x_m denote the values of r and x at a point where the diameter is a maximum.

A steady flame was obtained by passing the coal-gas and air from an ordinary Bunsen burner through a box containing baffle-plates to thoroughly mix them. The mixed gases were burnt from a vertical brass tube about half an inch in diameter. A brass tube about $\frac{7}{8}$ inch in diameter and 3 inches long was supported so as to be concentric with the first tube, and the top of this second tube was about one inch higher than the top of the other. The inner cone of the flame was just below the top of the outer tube. This arrangement gave a very steady flame the diameter of which was nearly constant for 3 inches above the burner. The outer tube prevented the wobbling of the flame. A small bead of the salt to be investigated was supported on a platinum wire about 1 cm. above the tip of the inner cone. Two fine platinum wires supported on adjustable stands were adjusted so that their ends just touched the surface of the region emitting visible light at opposite ends of a horizontal diameter of its widest part. The distance from the bead to the end of either wire was measured, and also the distance between the ends of the two wires. These distances are r_m and $2y_m$. We have then $x_m = \sqrt{r_m^2 - y_m^2}$.

To find the coefficient of diffusion of the salt vapour we require also to know the velocity of the flame gases. Small luminous particles moving up the flame could be seen to travel along parallel vertical straight lines for several inches above the burner. The velocity was found by means of a

bead of sodium sulphate which was supported on a wire attached to one prong of a vibrating tuning-fork. The fork also carried two small screens between which the flame could be seen once in each vibration of the fork. The salt vapour from the vibrating bead when observed through the screens had a wavy outline, and the wave-length was measured. The wave-length multiplied by the number of vibrations per sec. gives the upward velocity of the flame. In this way the velocity was found to be about 200 cm. per sec.

The experiments do not admit of much accuracy because it is difficult to set the platinum wires on the rather hazy boundary of the region emitting light. After some practice, however, independent values found for K did not differ by more than about 10 per cent.

In addition to the region emitting light which surrounds the bead, there is a separate region which forms a sheath covering the outside of the flame. This extends from the top of the flame down to a few centims. above the bead. This outer sheath obscures the upper part of the inner region and makes the observations more difficult. Very often the inner region is not the same colour as the sheath. The caesium and lithium salts available contained some sodium, and the bright coloration due to it made it difficult to set the wires on the edge of the coloration. In the case of the lithium salt the red colour was outside the sodium yellow, so that it did not matter much, but the caesium coloration was badly obscured.

The following table gives the values found in centims. for the distance from the bead to a point on the widest part of the inner region emitting light (r_m) and the width of the widest part ($2y_m$). Each number is the mean of several determinations.

	r_m .	$2y_m$.	K.
Lithium	2.4	1.6	14.5
Sodium	2.0	1.3	11.5
Potassium	2.0	0.85	4.7
Rubidium	1.9	0.80	4.4
Cæsium	1.9	0.80	4.4

It appears that caesium, rubidium, and potassium salt vapours diffuse at nearly equal rates, while sodium and lithium diffuse more quickly. The velocity of the positive ions of alkali salt vapours in flames appears to be about 60 cm. per sec. for 1 volt per cm.* at high temperatures.

* H. A. Wilson, Phil. Trans. A. vol. cxcii. p. 499 (1899).

If these ions consist of atoms of the alkali metal, and if we suppose that the light emitted also comes from atoms of the metal, then we can calculate the charge carried by the atoms of the metal in the flame. We have the well-known equation

$$\frac{ne}{p} = \frac{k}{K},$$

where e is the charge carried by one ion, n the number of molecules per c.c. in a gas at pressure p , k the ionic velocity, and K the coefficient of diffusion of the ions. If the metal atoms are only charged part of the time, then the observed value of the velocity will be kf , where f is the fraction of the time during which the atom is charged.

We have therefore $kf=60$. Hence for alkali salts in the flame

$$ne = \frac{60p}{Kf}.$$

In a previous paper I have given values of f deduced from the observed conductivities of flames containing salt vapours. The values found were

Cæsium	0.99
Rubidium.....	0.96
Potassium	0.91
Sodium	0.41
Lithium	0.21

Taking the temperature of the flame to be 2000° C., we get

$$n_0e = 1.8 \times 10^4 \times \frac{2273}{273} \times \frac{p}{Kf}$$

in electrostatic units, where n_0 denotes the number of molecules per c.c. in a gas at pressure p and at 0° C.

Taking $p = 1.01 \times 10^6$ dynes per sq. cm., we get the following values of n_0e :—

	$n_0e.$	$n_0e \div 1.3 \times 10^{10}.$
Cæsium	3.47×10^{10}	2.67
Rubidium	3.58 „	2.75
Potassium	3.53 „	2.71
Sodium	3.21 „	2.47
Lithium	4.96 „	3.81

If we omit f in the expression for n_0e , we get the following for the average values over a long time of $n_0e \div 1.3 \times 10^{10}$:

Cæsium	2.64
Rubidium.....	2.64
Potassium.....	2.47
Sodium	1.01
Lithium	0.80

1.3×10^{10} is the value of the charge carried by the molecules in 1 c.c. of any gas at 0° C. and 760 mm. pressure, if each molecule carries the charge on one hydrogen ion in a solution.

It appears therefore that the average charge on lithium and sodium atoms in the flame is about equal to that on hydrogen ions in solutions, while the average charge on cæsium, rubidium, and potassium atoms is nearly three times greater.

It seems quite reasonable to suppose that alkali metal atoms which are very strongly electropositive should at the high temperature of the flame lose several electrons. In hot air at about 1400° C. it was shown by the writer that each atom of the alkali metals carries the same charge as that on one hydrogen ion, but the flame is certainly much hotter than 1400° C., and also the violent chemical actions in the flame might be expected to favour the escape of more electrons.

The well-known formula $k = e\lambda/mv$, where e is the charge on one ion, λ its mean free path, m its mass, and v its velocity of agitation, gives values of k for cæsium several times less than the observed value 60 when e is taken to be the same as that on one hydrogen ion in a solution. If we take e to be three times that on one hydrogen ion, then the formula $k = e\lambda/mv$ gives a value nearly equal to 60 for a cæsium ion. Very little weight, however, can be attached to this coincidence, because the formula $k = e\lambda/mv$ is probably only very roughly true, and also the value of λ is not known for alkali metal atoms in the flame. It has to be merely guessed at, and may easily be wrong by a factor of two or three. Also recent theoretical investigations indicate that the velocity of ions heavier than the surrounding gas molecules should be nearly independent of their mass. This agrees with the nearly equal ionic velocities and coefficients of diffusion found for cæsium, rubidium, and potassium.

As to sodium and lithium, the fact that their coefficients of diffusion are larger also agrees with the theory, for their masses are less than that of the molecules of the flame gases. That their ionic velocities are not also larger appears to be due to the fact that they are only ionized part of the time,

so that the velocity observed is only an average, and is less than the velocity would be if they were charged all the time.

In conclusion, it may be said that the results obtained on the ionic velocities, coefficients of diffusion and conductivities of salt vapours in flames, seem to agree with the view that the positive ions consist of metal atoms having charges about three times the charge on one hydrogen ion in solutions. At the same time it must be pointed out that the possible error in the determinations of all these quantities is large; so that it is possible, but I think improbable, that the charge per ion is in reality equal to that on one hydrogen ion.

In a previous paper I gave reasons for believing that the positive ions due to salt vapours in flames are atoms of the metal. The arguments used in that paper are independent of the value of the charge carried by each ion so long as all the atoms when ionized carry the same charge. It has been suggested by Langevin that these ions are hydrogen atoms. This suggestion depends entirely on calculations of the ionic velocity by means of the formula $k=e\lambda/mv$. This formula cannot be relied on to give the velocity within a factor of at least two or three, partly owing to our ignorance of the true values of λ and partly because the formula itself is unreliable. No suggestion has been made as to how hydrogen ions are produced by salt vapours; and moreover the experiments made to determine the ionic velocities cannot be explained satisfactorily on the view that the ions are hydrogen atoms. Also salt vapours produce enormous conductivity in flames which contain no hydrogen. The increases of current observed in the determinations of the ionic velocities are nearly proportional to the conductivities due to the salt vapours, which shows that the ionic velocities measured are not those of a few special ions produced by some secondary reaction, but are the velocities of the majority of the ions due to the salts which must be formed from the salts, and therefore cannot be hydrogen.

IX. *On the Existence of Chemical Compounds of Short-lived Radioactive Elements.* By HANS SCHRADER, Ph.D.*

Introduction.

THE short-lived radioactive transformation products of radium, thorium, and actinium, which are included under the name of active deposits, do not differ fundamentally in their physical properties from the elements of

* Communicated by Prof. E. Rutherford, F.R.S.