COEFFICIENTS OF DIFFUSION OF CERTAIN ALKALI SALT VAPORS IN THE BUNSEN FLAME

BY GEORGE E. DAVIS

ABSTRACT

The method used is a modification of one suggested by H. A. Wilson. The ellipsoidal streak of luminous vapor from a salt bead held in the flame, was photographed; then the coefficient of diffusion K was obtained from the equation $K = \frac{1}{2}rv(dx/dr - 1)$, where r is the radial distance from the bead to a point on the boundary of the streak, x is the vertical distance of the point above the bead, and v is the velocity of the flame gases. A Meeker gas burner of special design was used, supplied with air under pressure and with intermittent puffs of salt spray to enable v to be determined. The flame temperature, determined by Féry's method, was 1436°C. The means of about ten determinations of K for each salt are: *lithium chloride*, 12.4; *lithium sulphate*, 9.7; *sodium chloride*, 19.0; *sodium sulphate*, 16.4; *potassium sulphate*, 11.1; *rubidium sulphate*, 11.7; *caesium sulphate*, 8.4. These are probably accurate to about 10 per cent. The chlorides of both Li and Na diffuse faster than the sulphates. Except in the case of the lithium salts, for which the observed values are relatively too low, the diffusion coefficients increase roughly as the reciprocals of the square roots of the weights of the metal atoms, also roughly as the reciprocals of the square roots of the molecular weights. If the free metal atom of the salt is the source of luminosity, as some other experimenters have concluded, it is probable that it is free only a fraction of the time, the fraction varying with the salt and the alkali.

IN 1912, H. A. Wilson published the results of some measurements of the coefficients of diffusion of alkali salt vapors in the Bunsen flame.[1] Some time later, while working under the direction of Prof. Wilson, the author made some new measurements of the coefficients of diffusion of a number of salts, including certain salts of the alkali metals. In these determinations, the data obtained for any one salt were not enough to make the result very reliable. More recently a new series of measurements has been carried out. A photographic method suggested by Prof. Wilson is used, with certain modifications which simplify the calculations and increase the accuracy of the results.

THEORY

The streak of luminous vapor extending upward from a bead of salt held in the non-luminous Bunsen flame appears to the eye to have a rather well defined boundary. This apparent boundary is the locus of

---

[1] H. A. Wilson, Phil. Mag., July 1912

points at which the concentration of salt vapor is equal to the minimum value for visible luminosity. Therefore the concentration is the same at all points on this boundary. In the paper published by Wilson in 1912,[1] it is shown that the concentration C at any given point at a distance r from the salt bead is given by

$$C=\frac{q}{4\pi Kr}e^{(v/2K)(x-r)}\ , \tag{1}$$

where q is the amount of salt evaporating in unit time, K is the coefficient of diffusion, v is the velocity of the flame gases, and x is the distance to the given point measured along the axis of the flame. From the graph of this equation we find that any surface of constant concentration resembles an ellipsoid of revolution with its major axis lying along the axis of the flame. Hence the apparent boundary of the luminous streak of salt vapor should be such a surface. Expressing r in terms of x and y, in Eq. (1), differentiating with respect to x, and setting dy/dx equal to zero, gives

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

where r_m and x_m are the values of r and x where the horizontal diameter of the streak is maximum. Wilson observed x_m and the maximum diameter of the streak directly and computed K by Eq. (2). The principal objection to this method is that the maximum diameter of the luminous streak is very difficult to observe and locate definitely by direct observation.

In the experiments performed under the direction of Prof. Wilson, referred to above, a different equation was used. From Eq. (1) we may obtain

$$K=\frac{v(x_2-x_1-r_2+r_1)}{2\log(r_2/r_1)}\ , \tag{3}$$

where the subscripts refer to any two given points on the apparent boundary of the luminous streak. The values of x and r were obtained by photographing the luminous streak and taking measurements on the photographic plate. An average value of K was found from the results for several pairs of points.

In the present measurements a still different equation was used. Differentiating Eq. (1) with respect to r, we get

$$K=\frac{rv}{2}\left(\frac{dx}{dr}-1\right)\ , \tag{4}$$

which holds for points on the apparent boundary of the luminous streak. Values of x and r were obtained from the photographic plate, as before. These values were plotted and the slope dx/dr obtained from the resulting curve for a number of points corresponding to a chosen series of values of r. For such a series of points, we obtain from Eq. (4)

$$K = \frac{v}{2\,(1/r)_{av}} \left[\left(\frac{dx}{dr}\right)_{av} - 1 \right] .$$

Comparing this with Eq. (4), it is seen that for the average slope there is a corresponding value of r, say $\bar{r}$, equal to the reciprocal of the average value of $1/r$ and independent of K and v. $\bar{r}$ and the average value of dx/dr were substituted in Eq. (4) for r and dx/dr, respectively. This method of averaging values makes only one substitution in the equation necessary. The same value of $\bar{r}$ can be used for a number of different curves.

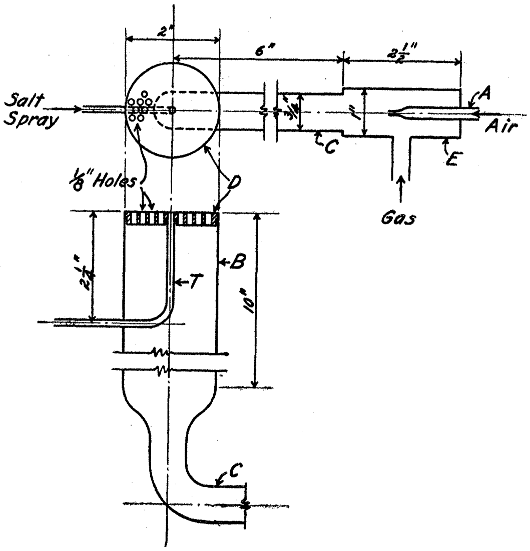

FIG. 1. Gas burner

EXPERIMENTAL METHOD

In order to obtain a large gas flame, a Meeker type of burner of special construction was used (Fig. 1). A large number of holes were drilled close together in an iron disk D. This formed the burner top. B is a vertical brass tube, joined to a smaller horizontal tube C. The chamber E consists of an iron tee connected with the air intake tube A by means of reducing fittings. Compressed air was used. Tube *A* was arranged as shown in order that the air pressure might not force the gas back. The long length of tubes *B* and *C* allowed the gas and air to mix thoroughly before being burned. Shorter lengths, with baffle plates as mixers, were tried, but were found impractical because of the tendency of the flame to "strike back." A tube (*R*, Fig. 3, not shown in Fig. 1) 5 in. long, diameter 2.5 in., was supported so as to be coaxial with tube *B* and extend about .75 in. above the burner top. This tube helped to steady the flame. The flame appeared to be perfectly uniform and did not taper much for a distance of several centimeters above the burner. The small tube *T* was used to introduce puffs of salt spray into the flame in order to measure the velocity of the flame gases.

To obtain these puffs of salt spray, a special type of valve (Fig. 2) was designed. *C* is a cylindrical chamber made by drilling out a solid brass cylinder. *D* is an iron disk screwed onto the end of a shaft *S* fitted with sleeve and set screws (not shown) for connecting with the shaft of an electric motor. Face *f* of disk *D* is machined smooth and made accurately perpendicular to the axis of *S*. The inner face *f* of the cylinder end also is turned smooth and is held against *D* by means of spring *P* which carries a small pivot *V*. This arrangement allows *S* and *D* to turn freely without imparting much torque to *C*. Near the circumference of *D* are drilled 8 small, evenly spaced holes *h*, so placed as to come in turn into momentary alignment with the hole through nipple *B*, as *D* rotates. The opposite end of chamber *C* is closed by a brass disk *K* which carries a nut *N* and a nipple *A*, all machined from the same piece. When in use, the barrel *C* is supported by a rubber band placed around it, which keeps *C* from turning yet takes up slight movements due to lack of perfect alignment of shaft *S* with the motor shaft. Salt spray entering through *A* passes out at *B* in a series of puffs as disk *D* rotates. These puffs are led into the flame through tube *T* of Fig. 1.

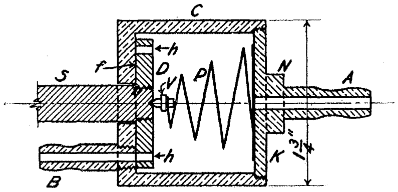

FIG. 2. Valve for giving puffs of salt spray

The general arrangement of apparatus is shown in Fig. 3. *W* is a platinum wire with a very small loop at the end, holding a salt bead *B* in the center of flame F as seen from above. The section of W heated by the flame was adjusted so that only the salt bead showed on the photographic plate when an exposure was taken with camera C. S is a vertical steel millimeter scale with its edge nearest B located in the plane which passes through B perpendicular to the axis of the camera lens. A Bausch and Lomb achromatic lens was used, diameter of full aperture $1\frac{5}{8}$ in. It gave an image free from distortion, using full aperture. Panchromatic plates were used. Adjustment was made for nearly equal size of object and image.

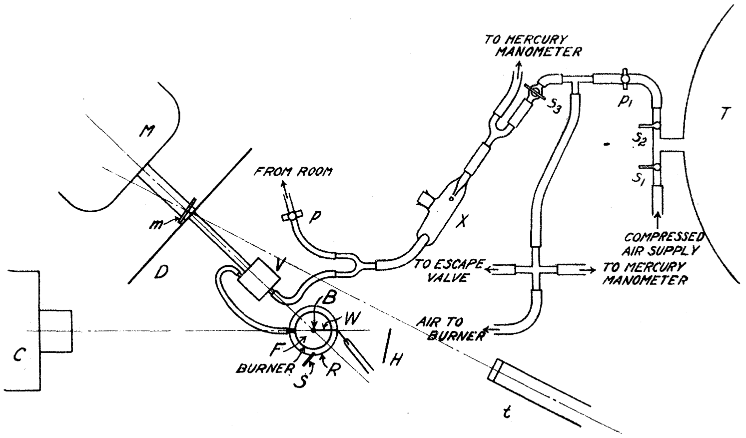

FIG. 3. General arrangement of apparatus

Connections were made with the compressed air line as shown. A tank T of about 12 cu. ft capacity helped to steady the flow. The pressure of the air going to the burner was regulated by a special type of escape valve, the essential parts of which are shown in Fig. 4. This consisted of a brass tube A working easily but snugly inside a second tube B. Melted lead poured into A closed the upper end and furnished part of the necessary weight. Adjustment of weight was effected by adding lead shot. Vaseline was used to lubricate the movable tube and prevent the escape of air between the tubes. Tube A had a number of very small holes drilled through it in two vertical rows located opposite each other. The action of the valve as a pressure regulator is obvious. It kept the pressure constant within a range of 1 or 2 cm of mercury. It was supplemented by hand regulation when necessary, using stopcock S_1 and pinchcock p_1 (Fig. 3). As a rule, the air pressure was adjusted to about 30 cm of mercury. Then the gas pressure was adjusted until the inner cones of the flame were just below the height at which they flared up. These conditions were kept as nearly constant as possible in all the determinations. Mercury U-tube manometers were connected as shown. A tilted U-tube with water in it indicated the pressure in the gas line (not shown).

The velocity of the flame gases was determined as follows. Compressed air was let into atomizer X by opening stopcock S_3. Salt spray, from a solution of sodium chloride in X, passed partly to valve V (previously described) and partly through a tube leading out of the room. The shaft of V was connected directly to the shaft of an electric motor M. The motor shaft also carried a 10 in. metal disk D with 8 evenly spaced radial slits cut in it. When D and the disk of valve V were rotated, 8 puffs of salt spray were introduced into flame F per revolution. Viewed through the 8 slits in D, conveniently by means of mirror m, these puffs appeared to be stationary in the flame. The distance between puffs was measured by use of a cathetometer with telescope t. H is a screen for t. Settings on the puffs were made where their diameters were largest. Three puffs were visible at one time. Multiplying the speed of the motor in r.p.s., determined with a revolution counter, by 8 times the distance between puffs, gave the velocity of the flame gases.

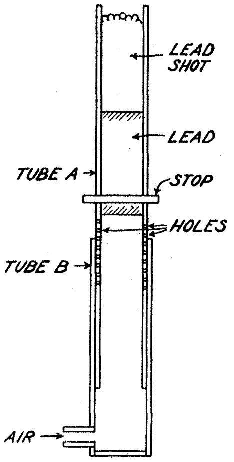

FIG. 4. Constant pressure air valve

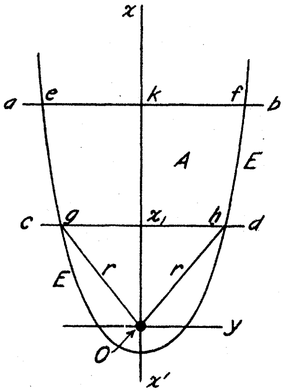

FIG. 5

The temperature of the flame was found by Féry's method,[2] using the carbon filament of an incandescent lamp as the body whose temperature is adjusted to that of the flame. Adjustment was made for reversal of the sodium D-line. The filament temperature was measured by means of a Leeds and Northrup optical pyrometer. As a check upon results, readings also were taken on the flame from an ordinary Bunsen burner.

---

[2] Féry, Comptes Rendus, **137**, 909-912 (Nov. 30, 1903)

These latter readings fell above the scale limit of the pyrometer but could be estimated without much error.

All the experiments were performed in a darkroom. The waste flame gases and salt vapor were led out of the room by a flue made of 6 in. stove pipe, supported with the lower end directly over the flame.

Several photographic plates (on the average eight) were exposed during each run, without allowing the flame adjustment to change. Usually two or more different salts were represented in each such group of exposures. This made possible a more accurate comparison of the coefficients of diffusion of the various salt vapors.

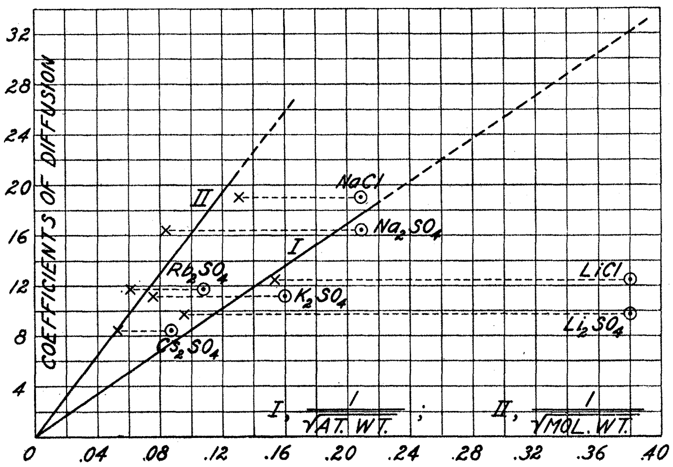

Fig. 6. Coefficient of diffusion of salt vapor as function of reciprocal of square root of weight of metal atom (I), and of molecular weight (II).

The method of marking the plates was as follows. Referring to Fig. 5, the center of the image *O* of the salt bead was first marked with a needle prick. Then a line *ab* was cut across the image *A* of the luminous streak as far from *O* as the distinctness of the apparent boundary *EE* of the streak would allow. This line was cut as nearly perpendicular to the axis *xx′* as could be judged before the axis was located. The points *e* and *f* where the line met the boundary *EE* were then marked, *ef* carefully bisected, and a line *xx′* cut through the middle point *k* and the center of the bead. Then the plate was put on the table of a dividing engine and from 7 to 15 evenly spaced lines like *cd* cut 2 or 3 mm apart, perpendicular to *xx′*, above *O*. The points where these lines met the boundary *EE* were then marked. In many cases the image *A* faded out quite gradually at the edge, so that it was somewhat difficult to locate these points. In locating them, some consideration was given to the fact that the theory of diffusion indicates that the points should fall on a smooth curve on either side.

A different method of locating points of equal intensity of blackening was tried, using a microphotometer of the form described by Meggers and Foote,[3] and considering points near the apparent boundary *EE*. This method seemed to promise more accurate results than could be obtained by the method of marking just described. However, the results actually obtained were often inconsistent and unsatisfactory, so the method was not used.

To measure the plates, they were placed on a small table carried by the movable table of a dividing engine and viewed by means of a fixed microscope mounted above. Distances could be read accurately to .001 cm. The distance (as *gh*, Fig. 5) from edge to edge of the image of the luminous streak was measured along each of the cross-lines and the corresponding radial distance r calculated. The distance representing unit length on the plate was obtained by taking a series of readings on the image of a scale appearing on the plate along the image of the luminous streak. Incidentally it was found that interposing a sheet of reddish-brown glass between illuminator and plate made the images on the plate stand out much more clearly than when illuminated by white light.

Next, x was plotted against r on accurately ruled paper of large size. The curves were from 45 to 80 cm in length. They were very carefully drawn and the plotted points usually fell on, or very close to, a smooth curve. The coefficient of diffusion of the salt vapor was obtained from the curve by the method described under "Theory." The values of the slope dx/dr were found by laying a straight-edge tangent to the curve at the chosen points. This could be done with a fair degree of accuracy, since the curves were very nearly straight in every case.

It is assumed in the mathematical theory that all the stream lines of the moving medium are parallel. Therefore it is important to determine whether the tapering of the flame and the distortion of the stream lines near the salt bead have an appreciable effect upon the results. As a test, a group of 25 plates giving long x, r curves were chosen at random. Two determinations of the diffusion coefficient K were made from each curve, one from the upper 5 values of r in the series already chosen, and one from the lower 5. Then the average K obtained from the upper points was compared with that from the lower. As a further test, two groups of 4 plates each were chosen, in each group the kind of salt and the flame

[3] Meggers and Foote, Scientific Papers Bur. Standards, No. 385 (June 30, 1920)

velocity being the same for all the plates. From the average dimensions in each group, a curve was plotted to represent the apparent boundary of the image of the streak of vapor. This curve was compared with a theoretical curve which had arbitrarily been made to coincide with it at two points. The results are given below.

EXPERIMENTAL RESULTS

In Table I is shown a typical set of values of dx/dr obtained from one of the x, r curves. In Table II are given the results obtained from the individual photographic plates, with their averages. The results obtained by H. A. Wilson are shown for comparison. The particular salts used in his determinations are not mentioned in his article, so are not specified here.

In Table III are shown the temperature readings at three different points in the flame, under different conditions as to pressure of air supply to the burner. Since the air pressure determines the velocity of the flame gases, the measurements show that the temperature was not appreciably affected by velocity variations much greater than those occuring during the determinations of the diffusion coefficients. The temperature is the same at all three points in the flame, within the limits of accuracy of the measurements. These points are so located as to give a fair indication of the temperature throughout the region in which the coefficients of diffusion were determined. Therefore we conclude that the results were not appreciably affected by variations in temperature from point to point in the flame. The average value, 1436°, may be a little lower than the true temperature, since the carbon filament used in the measurements was not a perfect black-body radiator. The true temperature may be from 45° to 90° higher.[4] However, the value 1850° for a Bunsen flame of the ordinary type agrees well with the most reliable values found by other observers.

The gas burned was manufactured from bituminous coal and may be described as a mixture of coal gas and "water gas." Its composition varied somewhat from day to day, as shown by analyses made by the department of chemistry. These analyses showed the following content, in volume per cent: CO, 11 to 16; CO_2, 4 to 7; O_2, 1.5 to 6; unsaturated hydrocarbons, 6 to 17; CH_4, 11 to 16.5; H_2, 18 to 21; N_2, 27 to 32.

In the first test made to determine whether the values found for the coefficients of diffusion K were affected appreciably by lack of parallelism of the stream lines of the flame gases, the average value of K for the

---

[4] Burgess and LeChatelier, "Measurement of High Temperatures"; observations by Burgess, pp. 340, 341.

upper 5 values of r came out 4.8 per cent higher than the average for the lower 5. In the second test, comparing theoretical shapes of streaks of salt vapor with shapes experimentally determined, a small departure of the latter from the former was found in each case. These tests seemed to indicate an appreciable but rather small effect on the values found for K, due to lack of parallelism of the stream lines.

TABLE I

Typical set of results

r	x	dx/dr*
.800	.614	1.068
1.000	.825	1.053
1.200	1.035	1.040
1.400	1.243	1.035
1.600	1.450	1.033
1.800	1.656	1.030
2.000	1.862	1.028
2.200	2.068	1.023
2.400	2.273	1.020
2.600	2.477	1.018
2.800	2.680	1.015
3.000	2.884	1.013
		Average $dx/dr = 1.031$

Reciprocal of average value of $1/r = 1.616$. Velocity of flame gases = 328 cm/sec. Coefficient of diffusion computed by Eq. (4) = 8.2.

* These values were obtained from a plotted curve, not computed from the values of r and x.

TABLE II

Coefficients of diffusion

	LiCl	Li_2SO_4	NaCl	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
	12.7	12.0	18.8	16.3	12.9(3)	11.7	8.2
	14.5	12.9	22.6	18.7	17.1	11.1	8.5
	15.0(3)	10.8	15.8(4)	14.8	14.2	13.7	8.7
	16.6	10.2	20.8	20.9	12.5	11.4	9.0
	11.9	11.1	22.9(4)	21.8	8.6	11.3	7.8
	10.9(4)	6.7	19.5	15.7	9.5	13.1(3)	9.6
	9.3	8.4	14.0	14.8	8.7(4)	10.6(4)	7.5
	15.3	9.6	19.2	13.3	9.1(4)	12.0	8.0
	10.8	8.5	18.6	15.4	6.3(4)	10.3(4)	8.0
	11.9	6.5(4)	15.8(4)	13.7			
	7.9	8.9(3)	20.4	14.6			
Weighted average*	12.4	9.7	19.0	16.4	11.1	11.7	8.4
Average deviation	±2.2	±1.6	±2.1	±2.3	±2.8	± .8	± .5
Wilson's results†	(Li)14.5		(Na)11.5		(K)4.7	(Rb)4.7	(Cs)4.4

* Scale of weights, 3 to 5; the weight is 5 unless otherwise indicated by figures in brackets; weighted on basis of excellence of photographic plate and apparent reliability of data.

† The particular kind of alkali salt examined in each case is not stated by Wilson.

TABLE III

Flame temperatures, by Féry's method

Position in flame	Pressure of air supply	Temperature
Lower center of flame, just above salt bead	18.3 cm Hg 30.8 31.1	1435°C 1440 1433
.8 cm from boundary of flame, just above level of salt bead	30.9	1426
Center of flame, about 2.5 cm above salt bead	30.9 49.0	1444 1440
		Av. temp. = 1436°

Reading on Bunsen flame of ordinary type, with full air supply = 1850°.

DISCUSSION

The coefficients of diffusion found in these measurements (Table II) do not agree well with those found by Wilson. It is believed that the results obtained in the present measurements are the more reliable for reasons given under Theory. A difference in composition of the gases burned in the two flames, or a difference in flame temperatures, may partly account for the disagreements. The above results are probably accurate to about 10 per cent.

It has been shown by Smithells, Dawson and H. A. Wilson[5] that the light emitted by a flame containing vapor of an alkali salt is probably due to atoms of the alkali metal. They pointed out that a metal atom might lose one or more electrons under the influence of violent collisions with other atoms in the flame, thus becoming a positive ion; and that this ion, upon recombination with other free electrons in the flame, might be subject to internal vibrations which would give rise to the radiation of light. This theory was strengthened by the results of later experiments by H. A. Wilson.[6] These experiments showed (1) that the luminous vapors of salts in a Bunsen flame are not deflected appreciably by an electric field; (2) that the positive ions present in the luminous vapor can be made to move out of it by an electric field; (3) that the positive ions are not luminous, but can form luminous vapor after recombination. It has also been shown by Bancroft and Weiser[7] that many metallic salts are dissociated in the Bunsen flame, the metal atom being set free.

---

[5] Smithells, Dawson and H. A. Wilson, Phil. Trans., A **193**, 89 (1899)

[6] H. A. Wilson Phil. Trans., A **216**, 63-90 (1915)

[7] Bancroft and Weiser, Journal of Phys. Chem., 1914.

If, as this evidence indicates, the metal atom of the vapor is the source of light, we might expect the coefficient of diffusion, determined from the shape of the luminous streak of vapor from a salt bead, to be the coefficient of diffusion of the free metal atoms. But it is likely that these atoms, because of their tendency to combine with other ions (radicals) in the flame, are free only part of the time. Therefore the average rate of diffusion for any particular atom probably is less than the rate we should expect if the atom were free during the whole of its journey. It therefore seems reasonable to assume that our observed values for the coefficients of diffusion are lower than the values for free metal atoms.

It is interesting to examine our results in the light of two different assumptions: (1) That the metal atoms were free during the entire time spent in diffusing; (2) that the molecules of salt vapor remained undissociated practically the entire time. In the first case, kinetic theory indicates that the observed diffusion coefficients should vary directly as the reciprocals of the square roots of the weights of the metal atoms. In Fig. 6, curve I, these quantities are plotted against each other (points marked with circles). In the second case, the observed coefficients should vary as the reciprocals of the square roots of the molecular weights of the salts. Plotting these quantities, we obtain curve II (points located by crosses). In either case, the values for the sodium, potassium, rubidium and caesium salts locate, roughly, a straight line passing through the origin, as we should expect. On the other hand, lithium chloride and lithium sulphate do not fall near the line located by the other salts in either case, their observed coefficients of diffusion being only roughly 1/3 and 1/2 the values indicated by curves I and II, respectively. The degree of accuracy with which each curve is located by its set of five points is about the same for the two cases. Again, the positions of the two sodium salts relative to a straight line drawn between them from the origin, depend on whether assumption (1) or assumption (2) is made. The same is true of the two lithium salts. These facts suggest that neither assumption is correct, but that the metal atoms are free part of the time and combined with other particles the rest of the time. As to the two lithium salts, their relatively low rates of diffusion may be due to diffusion of the particles in groups rather than singly.

Partial dependence of the rate of diffusion upon the negative radical of the salt is shown by the observed differences between the chlorides and the sulphates of lithium and sodium. In each case the chloride diffuses more rapidly than the sulphate of the same metal. The differences seem too large to be attributed to experimental errors alone. Referring to

Table II, we see that 4 values obtained for lithium chloride are higher than the highest value for lithium sulphate; while 7 values for sodium sulphate are lower than the lowest value for sodium chloride except one.

The various chemical and physical phenomena which occur in the flame are not yet well enough understood to warrant drawing more definite conclusions.

It is a pleasure to the writer to acknowledge indebtedness to Professor L. B. Spinney for his kindness in securing the necessary equipment for this work; also to Professor G. E. Thompson and especially to Professor J. W. Woodrow, for many helpful suggestions.

LABORATORY OF PHYSICS,
IOWA STATE COLLEGE,
AMES, IOWA.
March 8, 1924