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THE ABSORPTION OF LIGHT BY FLAMES CONTAINING SODIUM

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Abstract

The intensity of the light from flames containing sodium vapor was found to equal approximately $e/a_0\{(1+2a_0x)^{1/2}-1\}$, where x is the number of flames, e the amount of light that would be emitted per unit thickness, if no light were being absorbed, and a_0 is the coefficient of absorption for the sodium light at the beginning of its passage through the vapor. This expression is based on the assumption that the coefficient of absorption becomes less the further the light passes through the vapor. This may be expressed by the formula $a=a_0/(1+2a_0x)$, where a is the coefficient for light that has passed through x flames and a_0 is the value given above. The values found for e and a_0 were 2.06 and 4.33 respectively, where one flame into which a 0.1 percent solution of NaCl was being sprayed was taken as the unit of intensity of light. The light from flames into which different concentrations of NaCl were sprayed varied less rapidly than the square root of the number of flames. This is explained by assuming that with greater concentrations the molecules of salt in the flame are less completely dissociated, and that this is due to a constant dissociation and recombination of the sodium and chlorine atoms in the flame.

Introduction

When a number of flames into which a sodium salt is to be introduced are so placed that the light from each one passes through those between it and the measuring instrument, the light varies approximately as the square root of the number of flames and roughly as the square root of concentration of the salt being sprayed into them. However, experimenters differ as to the amount of the deviation from this square root law, as will be pointed out in following paragraphs. It, therefore, seemed desirable to repeat the measurements under varying conditions; and also to find, if possible, some explanation for this law which is in harmony with what is known concerning the absorption of such light by cold vapors.

Apparatus

Two methods were used in determining the intensity of the light. In the greater part of the work the light from a number of flames was compared with that from a single one by means of a Lummer-Brödhun photometer, the same mixture of air, gas and salt being used in the single as in the group of flames, so that any variation in the mixture would affect both in the same way. This method was found to be preferable to comparing the flames with some standard source because of the difficulty of producing flames at different times which have the same proportion of gas, air and salt solution. It was found that with the former arrangement the quality of the mixture could be changed quite appreciably without changing the comparative results obtained. The data obtained by this method were checked by measuring the intensity of the light with a photoelectric cell, as will be explained in a following paragraph.

For the greater part of the work gasolene gas was used. Both this and the air were forced through constricted tubes, so that their flow could be measured and kept constant. Small fluctuations in the pressure due to the pump were smoothed out by passing the air and the gas through large bottles. The salt was introduced by passing the air through sprayers containing a salt solution. For much of the work it was necessary to place three of these in parallel in order to furnish a sufficient amount of air. The windows of the photometer were covered with color filters which allowed no appreciable amount of light from the flames other than that from the sodium to pass through them.

In much of the work a bank of nine flames was used. This was made by inserting wing tops in a brass tube 3.2 cm in diameter. The flames were adjusted, so that as nearly as possible all were 3 cm wide at the bottom and 7 cm high. It was found that the flames could be made more uniform by bringing the gas through a small tube inside the larger one, and allowing it to escape from this one through a number of small holes. By this means the pressure was approximately the same at each of the tips. However, no method was found for measuring the size of the flames with sufficient accuracy to make it certain that all were of the same size and shape. Consequently they were all made as nearly the same as could be determined by the eye, readings were taken of different sets so adjusted, and the average of several such readings was taken. It is believed that the error of such an average is not sufficiently large to affect the general conclusions of this work. An opaque screen having its surface blackened was inserted between the flames when the light from only a part of them was being measured. The distance between the flames was 2 cm. It was found desirable to have them thus separated in order that they should not influence each other.

The effective distance between such a bank of flames and the photometer is not the same as the average distance, since the intensity of the light varies inversely as the square of the distance from the source, and since the light from the back of the group is largely absorbed by the flames in front. It can be shown that if they filled all of the space uniformly, and if the light coming from them varied as the square root of the number of flames, then the effective distance would be approximately the distance from the photometer to a point one-third of the distance from the front of the flames to the back. Experiments taken with flames at different distances from the photometer were in harmony with this conclusion. Consequently in this work the computations were made on the assumption that this was the correct distance to use. In the greater part of this work the distance as thus measured between the group of flames and the flame used for comparison was 80 cm.

In a few experiments screens, all of which had the same size of openings, were placed between the flames. However, these affected more or less the condition of the flames and gave more irregular results than those obtained without them, so that they were not used in obtaining the data which are here recorded.

DATA ON THE LIGHT FROM FLAMES

There are given in Table I data obtained by comparing the light from several flames with that from one. Such comparisons are made when different percentages of salt solutions were used in the spray. The mixture of air and gas was in each case as rich as it was possible to have it without the flame showing a continuous spectrum. Column 1 in this table gives the number of flames. The following columns give the relative intensities when solutions of 10, 1, 0.1, 0.05, 0.02, and 0.01 percent are used.

TABLE I.

No. of flames	10%	1%	0.1%	0.05%	0.02%	0.01%
1	1	1	1	1	1	1
2	1.52	1.54	1.57	1.66	1.70	1.71
4	2.31	2.27	2.37	2.50	2.58	2.73
6	2.84	2.84	2.92	3.21	3.56	3.85
9	3.5	3.5	3.71	3.87	4.26	4.73

These values are plotted in Fig. 1. The lowest curve in that figure gives the relative intensities as computed by the square-root law.

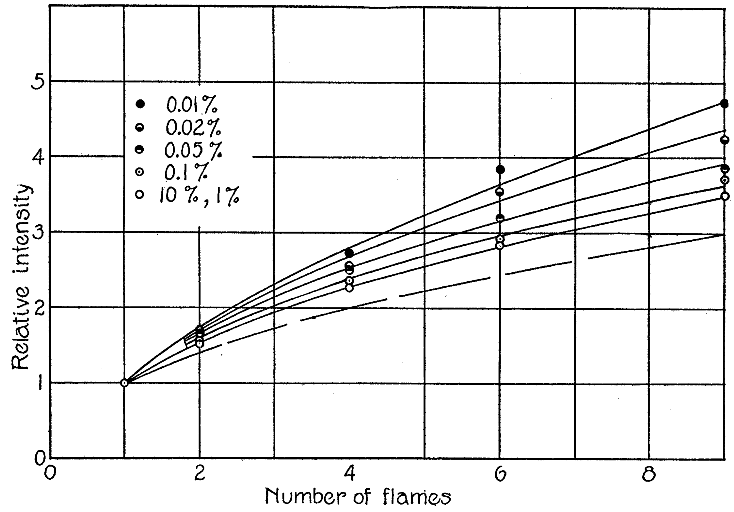

Fig. 1.

The curves with 0.02 and 0.01 percent solutions are less reliable than the others because of the difficulty of making observations with the very faint light given in such cases. The values for 10 and 1 percent were the same within the limit of errors of observation. With a saturated solution sprayed into the flames the same relative values were obtained as with a 10 percent solution.

The data given here are in approximate agreement with those of Locher[1] when small amounts of salt are sprayed into the flames. For more dilute

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[1] Locher, Phys. Rev. **31**, 466 (1928).

solutions the ratios are smaller, and for concentrated solutions they are larger than his. I did not, however, find any increase in the ratios in passing from 1 percent to 10 percent solutions as did Locher.

It is difficult to make a comparison with Gouy's[2,3] data, since he did not give the amounts of salt sprayed into the flames, but only the brightness, and while the brightness increases with the concentration of the salt, there is not a constant ratio between them. Moreover, Gouy confined his work to a comparison between one and two flames. His values for the ratio between the light from two flames and that from one, varied from 2 for the least luminous flames to a minimum of 1.38, followed by a maximum of 1.45, as the luminosity of the flames was increased. The minimum, no doubt, corresponded to that found by Locher with a 0.1 percent solution which I failed to find. In general, Gouy's values were smaller than those found by myself.

The difference between the data obtained by different experimenters can to some extent be explained as being due to a difference in the sprayers used. For example, a sprayer made by myself which was less efficient in breaking up the solution into a fine spray gave somewhat different values from those given in Table I.

RESULTS WITH THE PHOTOELECTRIC CELL

The preceding data were checked with measurements made with a photoelectric cell which was especially sensitive to radiations at the red end of the spectrum. This was used with a galvanometer giving 1 mm deflection for 1.5×10^{-10} amp. However, to obtain a deflection which could be measured conveniently it was necessary to place the cell not more than 20 or 30 cm from the group of flames, even when the stronger solutions were being sprayed into them. With these distances the uncertainty regarding the effective center of the flames made the measurements somewhat unreliable. As a result this method did not appear to be as trustworthy as those obtained with the photometer. It was, however, of value in checking the results already obtained, and as far as could be determined the two methods gave the same results. An explanation of these results will be suggested in a following paragraph.

FLAMES AT DIFFERENT TEMPERATURES AND WITH DIFFERENT SODIUM COMPOUNDS

Observations were made with common illuminating gas and also with acetylene gas mixed with gasolene gas. Hotter and more luminous flames were obtained with such gases, but as far as could be determined the ratios between the amounts of light obtained with different numbers of flames were the same as those found when gasolene gas alone was used.

Locher found different ratios when NaOH was used in the spray from those obtained with NaCl. The present writer could find no difference with the two solutions as long as the same amount of sodium was used with both.

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[2] Gouy, Ann. de Chimie et Physique **18**, 5 (1879).

[3] Gouy, Journ. de Physique **9**, 19 (1880).

Flames Containing Additional Chlorides

Amounts of HCl and NH_4Cl containing nine times as much chlorine as that in the original solution were added to one-tenth normal solution of NaCl. The HCl decreased the amount of sodium light about 22 percent and the NH_4Cl decreased it about 18 percent. These ratios do not, however, correctly represent the relative amounts of light actually emitted by the sodium atoms, since the absorbing powers of the flames are not proportional to the emitting powers, as will be discussed more fully in a later paragraph. In reality the ratios between the actual amounts of light emitted by the atoms with different solutions is larger than would appear from the preceding. A more accurate comparison is obtained by comparing the number of flames into which sodium chloride alone has been sprayed with one having an additional chloride. Thus 5.8 flames having NaCl alone is equivalent to 9 flames having also the above amount of HCl. That is, the addition of the HCl diminishes the emitting power of sodium atoms 35 percent. A similar determination showed that the addition of the NH_4Cl diminished the emitting power 28 percent. These measurements have not as yet been checked under varying conditions, so that they must be considered as approximations only.

Luminosity with Different Concentration

Wilson[4] and Locher[1] (p. 468) found that the light was the same whether a given amount of salt was sprayed into one or several flames, while Gouy[2] (p. 92) and Zahn[5] found it to be different. It therefore seemed desirable to obtain further evidence on this question.

The most satisfactory method of comparing flames into which different amounts of salt are sprayed was found to be the following. Two sets of such flames were compared by means of a photometer. The solutions in the two sets were then reversed, all other conditions being kept the same as before. The average ratio of the two sets was taken as the correct ratio. By this means any error due to a difference in the size or shape of the flames was eliminated.

For the sake of brevity the ratio between the luminosity obtained when a 10 percent solution was sprayed into a flame and that obtained with a 1 percent solution will be referred to in the following paragraphs as the "concentration ratio."

Effect of the Size of the Flames

It was found that the concentration ratio depends quite appreciably on the size of the flames being compared. It is, of course, difficult to measure the size of a flame accurately, so that the ratios found at different times vary somewhat, but the average results of several sets of observations with flames 4 cm wide at the bottom and 7.5 10, and 12.5 cm high gave concentration ratios of 2.7, 2.56, and 2.44 respectively.

Apparently this is due to the fact that the edges of the flames give a different ratio from that given by the centers. Thus it was found that when an

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[4] Wilson, Phil. Trans. Roy. Soc. **A216**, 63 (1916).

[5] Zahn, Verh. Deut. Phys. Ges. **15**, 1205 (1913).

opaque screen having an area of 2 cm^2 was placed in front of the central part of the flames 10 cm high, so that only the light from the edges reached the photometer, the concentration ratio was 2.73 instead of 2.6, the value previously obtained. On the other hand, when a screen in which there was an opening of 2 cm^2 was placed in front of the flames so that only the light from the central part reached the photometer, the ratio was 2.45. With larger flames a smaller proportion of the light comes from the edges, and consequently the ratio is smaller.

The ratio found when flames were compared into which 1 percent and 0.1 percent solutions were being sprayed was approximately 2.74. With solutions of 0.1 and 0.01 percent the ratio was approximately 3.3. The flames were 4 cm wide and 10 cm high. As has been explained when considering the addition of other chlorides these ratios do not represent the relative amounts of light actually emitted by the sodium atoms. A comparison similar to the one made there shows that approximately 5.3 flames with 0.1 percent solution give as much light as one flame of 1 percent solution. An explanation of this will be considered in a following paragraph.

Using sprayers which are less efficient in getting salt into the flame is equivalent to using weaker solutions, and no doubt causes some difference in the concentration ratio, but as far as could be observed any such difference was less than that due to experimental errors. Thus with each set of flames two sprayers were placed in parallel. Part of the time both sprayers were filled with solution, and part, one of them was empty so that air without any spray came through it. It could not be determined that there was any difference in the concentration ratios in the two cases. Ratios obtained when using sprayers made by myself gave the same results as those obtained with sprayers which had been purchased.

As far as could be determined the same concentration ratios were obtained with gasolene gas, city illuminating gas, and gasolene gas enriched with acetylene gas, providing the height of the flames was the same in each case.

The data which have been given were checked by measurements with the photoelectric cell, and the two methods showed good agreement. Any differences found were probably due to the difficulty in reproducing flames of a given size.

Explanation of the Data Observed

In general the values given here for what we have called the concentration ratios are much smaller than those given by Locher. These values taken with those on the relative intensities from different numbers of flames indicate that a given amount of salt when sprayed into one flame gives much less light than when sprayed into several flames, which is in agreement with the data given by Gouy and by Zahn.

The results obtained by Gouy which are here confirmed have been explained by Lenard[6,7] by assuming that with greater concentrations the mole-

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[6] Lenard, Ann. d. Physik (4) **17**, 238 (1905).

[7] See also Ladenburg and Minkowski, Ann. d. Physik **87**, 298 (1928).

cules of salt are less completely dissociated, so that more concentrated solutions produce less light than they would if the dissociation were always the same. Such an explanation is reasonable, but possibly does not go as far as it might. It seems probable that the dissociation is incomplete not because some of the molecules never become dissociated, but because there is a constant dissociation and recombination of the atoms of sodium and chlorine in the flame and that consequently the greater the amount of salt in the flame the more chlorine atoms there are with which the sodium atoms can combine, and the less the time the sodium atoms are uncombined. The strongest evidence of this is the fact that adding a chloride such as HCl or NH_4Cl decreases the amount of sodium light very appreciably, as has been shown. It is difficult to see how the presence of HCl can stop the dissociation of NaCl, but it is very easy to see how an additional number of chlorine atoms may cause a more frequent recombination of the sodium atoms with the chlorine, and thus cause a smaller proportion of the sodium to be dissociated at any instant with a corresponding decrease in the amount of light emitted.

If this is correct, then the presence of additional chlorine coming from an addition of NaCl would also cause less light to be emitted by the same amount of sodium. Thus it has been shown that a 1 percent solution in a single flame only gives as much light as 5.3 flames with a 0.1 percent solution. That is, the salt in a 1 percent solution is but little more than half as effective in emitting light as that in the 0.1 percent solution. This explanation seems the more probable since the addition of HCl produced roughly the same diminution in the efficiency of the sodium as an equal amount of chlorine introduced as NaCl, the decrease being 35 percent in the former and 47 percent in the latter case.

The dissociation probably occurs in two or more steps. Possibly the molecules break up into sodium and chlorine ions which then lose their charges becoming uncharged atoms. There may also be one or more intermediate steps in the recombination.[8] But certainly the sodium giving the light which we are studying consists of uncharged atoms, as is evident from its spectrum. Evidence that there are comparatively few charged sodium atoms in the flame is given by a study of the conductivity of flames. Wilson,[4] (p. 85) for example, estimates that only 1.6 percent of the sodium in a flame is ionized even when the concentration is small.

It also seems reasonable to assume that at the edge of the flame there is more complete dissociation of the salt than in the center, and that this is the cause of the difference between the concentration ratios obtained with light from the center and from the edges. A fairly definite proof that there is more dissociation at the edges is given by the appearances of a flame into which copper chloride is being sprayed. Such a flame gives almost no green color except at the edges, where it is a bright green. This is the more noticeable if there is a small amount of sodium impurity in the copper chloride. The center of the flame is then yellow with a distinct border of green.

The greater dissociation at the surface is no doubt in some way due to the

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[8] See Foote and Mohler's Origin of Spectra, p. 184.

greater amount of air there, but whether it is caused by a higher temperature or by a difference in chemical action can not at present be stated.

EXPLANATION OF DATA ON DIFFERENT NUMBERS OF FLAMES

The preceding data show definitely that the coefficient of absorption in the flames for the sodium light decreases rapidly as the number of flames through which the light has passed increases. A rough computation of this may be made by determining the ratio between the light which appears to be absorbed by any flame and that which enters it. For example, the light absorbed by the second flame equals the difference between that given by the first and second taken separately and that from the two taken together, or $2-1.54=0.46$, using one flame as the unit. The light absorbed by the ninth equals that obtained from eight flames plus that from the ninth, minus the light actually obtained from the nine or $3.43+1-3.68=0.75$. The apparent coefficient of absorption in the first case is 0.46 while that in the second is 0.25.

An explanation of the preceding follows from the assumption that parts of the sodium light are more easily absorbed than other parts. Probably the light at the center of the sodium lines in the spectrum is more easily absorbed than that at the edges. This may be expressed in other words by saying that the coefficient of absorption decreases as sodium light passes through the sodium vapor. A similar explanation was given by Hughes and Thomas[9] for the change in absorbing power of mercury vapor, and it is generally recognized that such action occurs when sodium light passes through cold sodium vapor.

In discussing the observed data it is of interest to consider a case which can be treated mathematically by assuming that the region between O and P in Fig. 2 is filled with a solid flame. Let x equal the distance OP. The light coming from the left and passing through the flame at the point P will, of course, be made up of light emitted by all the elements between O and P and not absorbed before reaching P. Let ΔI be the amount coming from the element $\Delta x'$ situated at a distance x' from P. Then

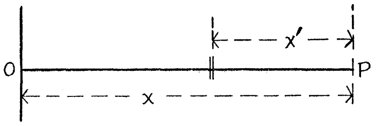

Fig. 2.

$$\Delta I = f(x')\Delta x' \tag{1}$$

and

$$I = \int_0^x f(x')\Delta x$$

where I is the total amount of light passing through the flame at P. By trying different expressions for $f(x')$ it was found that the assumption that

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[9] Hughes and Thomas, Phys. Rev. **30**, 470 (1927).

$$f(x') = \frac{e}{(1 + 2a_0x')^{1/2}}$$

where a_0 and e are constants whose significance will appear later, gives values for which I will agree closely with the observed data. Making this assumption we have

$$I = \int_0^x \frac{e}{(1 + 2a_0x')^{1/2}}dx' = \frac{e}{a_0}\{(1 + 2a_0x)^{1/2} - 1\}. \tag{3}$$

This becomes $I = e(2x/a_0)^{1/2}$ when a_0x is very large compared with unity. The light then varies as the square root of the number of flames. From (3) we would have

$$\frac{dI}{dx} = \frac{e}{(1 + 2a_0x)^{1/2}} \text{ and } \left.\frac{dI}{dx}\right|_{x=0} = e \tag{4}$$

e then is the rate at which I increases at the origin where the amount of light being absorbed is zero. In other words, e is the rate per cm thickness at which light is emitted by the sodium vapor.

Combining Eqs. (1) and (2) we have $\Delta I = e\Delta x'/(1+2a_0x')^{1/2}$. If we let a equal the coefficient of absorption at the distance from the point where the light starts we have

$$a = -\frac{(d/dx)\Delta I}{\Delta I} = \frac{a_0}{1 + 2a_0x'}\cdot \tag{5}$$

When $x=0$, $a=a_0$. That is, a_0 is the coefficient of absorption at the point where the light begins to be absorbed. In other words, the coefficient of absorption for the light from any element becomes less as it passes through the flames.

The expression $I = e/a_0\{(1+2a_0x)^{1/2}-1\}$ agrees closely with the observed data. If the light from a flame into which a 0.1 percent solution is being sprayed is taken as the unit for the intensity of light, x the number of flames, and if e is given the value of 2.06 and a_0 the value of 4.33, we obtain the numbers given in column 2 of Table II. Column 1 in this table gives the number of flames, and column 3 the observed values.

TABLE II.

No. of flames	0.1% Computed	0.1% Observed	0.01% Computed	0.01% Observed
1	1	1	0.298	0.302
2	1.55	1.57	0.510	0.516
4	2.36	2.37	0.831	0.825
6	2.98	2.92	1.09	1.16
9	3.74	3.71	1.41	1.43

The work on the relative intensities of flames into which different solutions are sprayed indicated that one flame into which a 0.1 percent solution is sprayed gives 3.3 times as much light as one with a 0.01 percent solution. It is also equivalent to 5.3 such flames. If then we substitute for x in Eq. (3),

$x/5.3$ and for I, $1/3.3$, we will obtain the theoretical values for the 0.01 percent solution flames. Such values are given in the fourth column of Table II, and the corresponding observed values in the fifth column. With both sets of flames there is close agreement between the observed and the computed values.

However, if the same kind of substitution is made for flames into which 1 percent and 10 percent solutions are sprayed, the computed values are smaller than the observed values. This discrepancy can be explained by assuming that a decreases more rapidly than is indicated by Eq. (5). However, no formula was found which is at all simple and agrees with the observed values any more closely than does this one. We may, therefore, conclude that the preceding equations represent a first approximation to the correct statement.

Numerical values of e and a_0, differing somewhat from those given above can be used which will still give numbers nearly the same as those in Table II. These values of e and a_0 can not, therefore, be considered as having been determined with any great accuracy. However, taking these values as they stand, it can be computed that if there were no absorption, the light which would be obtained from a single flame into which a 0.1 percent solution is sprayed would be 2.06 times that actually obtained, and from nine flames there would be 4.9 times that actually obtained. From a flame into which a 10 percent solution is sprayed the light would be 8.2 times that actually obtained, and from nine such flames it would be 21 times that actually obtained.[10]

Assuming that $a = a_0/1+2a_0x$ where a_0 is 4.33, we find that a equals 0.448 when x is 1. That is, the coefficient of absorption for light that has passed through a flame into which a 0.1 percent solution is being sprayed is less than one-ninth of what it was at first. Similarly after the light has passed through a flame into which a 10 percent solution is being sprayed the coefficient is less than 1 percent of what it was at first.

The assumptions here made are similar to those made by Hughes and Thomas, but are not identical. Thus we have here assumed that the light, unabsorbed after passing through x flames is $e/(1+2a_0x)^{1/2}$, while the results given by them are very nearly proportional to $10.8\times10^{12}/10.8\times10^{12}+n$ where n is the number of absorbing atoms. By choosing proper constants this can be written in the form $e/(1+2a_0x)$. That is, the first power of the denominator occurs in the expression as given by Hughes and Thomas, while in the expression here used for sodium atoms the same denominator is raised to the one-half power. Whether this is due to a difference between sodium and mercury vapor, to the very different conditions under which the observations were made, or to some other cause is not known. Considering all of the differences it is perhaps surprising that there is as much similarity as there is.

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[10] This is contrary to the conclusion reached by Foote and Mohler (Origin of Spectra, p. 167) who state that practically all of the photons produced by the sodium atoms in a flame are emitted from the flame. It would, however, appear to be impossible to reconcile the facts given here with their statement.