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TRANSITION PROBABILITIES AND QUENCHING IN THE 3*P* STATE OF SODIUM

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Abstract

The effect of foreign gases upon the fluorescence of sodium vapor excited by the second line of the principal series has been investigated. The gases used were helium, nitrogen, and hydrogen and the intensities of both the 3303A line and the *D* light were observed. From the variation in intensity of the 3303A line as gas is added it is concluded that the presence of an inert gas has no appreciable effect upon the relative transition probabilities in the 3^2P state of sodium. With nitrogen or hydrogen as the added gas the *D* light intensity variation followed that of the 3303A line very closely but with helium a marked increase in intensity was produced by the first gas added with a decrease at higher pressures. This increase was explained as due to a transfer of sodium atoms from the 3^2P to the 3^2D state by collisions, thus increasing the number of atoms which radiate the *D* light. In addition to this increase in number the collisional transfers produced an increased "Doppler width" in the *D* light which persisted up to pressures well over 100 mm of helium and caused a decreased absorption of the fluorescence light. The bearing of this work on the difference in the intensity ratio of the 2^2S-3^2P and 1^2S-3^2P transitions as reported by Weiss for an arc and by Christensen and Rollefson in fluorescence is discussed. It is concluded on the basis of experimental evidence that any explanation of the difference which depends upon multiplicity of the 3^2P state is incorrect. An explanation of this difference based upon the assumption that the life period of an excited atom varies inversely as the transition probability of the radiation emitted is presented. It is shown that recent work on the life periods of atoms in the 2^3S_1 state of mercury at least partially supports this assumption. A new type of sodium arc with increased intensity and stability of operation is described.

When transitions by radiation are possible from one energy level to two or more lower energy levels, the relative numbers of each of these possible transitions is designated by what is known as the transition probability. This transition probability has generally been assumed to be a constant, independent of the method of excitation or of the environment of the radiating atom.

Recent investigations concerning the transitions from the 3*P* state of sodium by Weiss,[1] by Christensen and Rollefson[2] and by Prokofjew[3] have seemed to indicate that the transition probabilities in this case are dependent upon either the method of excitation or the environment of the radiating atoms.

Figure 1 shows the different possible transitions from the 3*P* state of sodium. For convenience in discussion they are labelled (a), (b) and (c). The

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[1] Weiss, Ann. d. Physik **1**, 565 (1929).

[2] Christensen and Rollefson, Phys. Rev. **34**, 1157 (1929).

[3] W. K. Prokofjew, Zeits. f. Physik **58**, 255 (1929).

fine structure of the terms is not shown. The investigation by Weiss[1] concerning the radiation in a low-voltage arc shows the ratio of the probabilities of transitions (b) and (a) to be 25 to 1. The results of the investigation of Christensen and Rollefson[2] on the fluorescence of sodium vapor excited by the 3303A radiation from a sodium arc show this ratio to be 1.7 to 1. R. Ladenburg has made the suggestion that the method of correction for absorption used by Christensen and Rollefson may be in error due to the change in absorption coefficient with wave-length over the breadth of the line. With the formulas and tables presented in a paper by Ladenburg and Levy[4] the theoretical correction has been calculated. It is found that for the measurements taken with the center of the exciting cone at a depth of 3 mm approximately 80 percent of the *D* light should be absorbed while the absorption of the 3303A is too small to have any appreciable effect upon the calculation. If the data obtained by Christensen and Rollefson are recalculated and the theoretical correction for absorption introduced, a value of 5.7 is obtained.

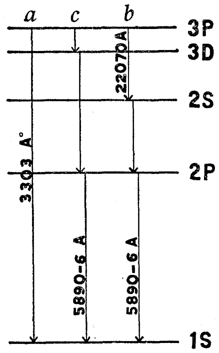

Fig. 1.

The calculation of this correction is, however, subject to serious errors due to the data upon which it was based. The experimental arrangement used by Christensen and Rollefson[2] was such that a fairly constant temperature could be maintained but no attempt was made to obtain an accurate measurement of the actual temperature of the fluorescence tube. A variation of approximately 15°C in the temperature produces a change of a factor of two in the vapor pressure of sodium. If the temperature used were fifteen degrees too high the correction for absorption would change to approximately 66 percent giving a ratio of 3.4. The data found for the vapor pressure of sodium itself do not agree within a factor of two.

That some error is involved is indicated by the fact that the ratios calculated from the data at two different depths differ by over twenty percent. The only experimental errors which might contribute to such a discrepancy are the photometric ones which do not exceed ten percent. If we assume that this discrepancy is due to an incorrect value for the vapor pressure of sodium and repeat the calculation for different pressures we find the same value for

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[4] Ladenburg and Levy, Zeits. f. Physik 65, 189 (1930).

both depths if we select the conditions so that the corrected ratio is 3.4. We feel that this represents the best value which can be obtained from the data.

The results of the calculations carried out by Prokofjew[3] based upon the methods of wave mechanics, give a value of 2.1 for the ratio of these two transition probabilities.

The value of this ratio calculated by Christensen and Rollefson on the basis of their measurements of the relative intensities of the 5890A and 3303A radiation in fluorescence depends upon the assumption that the probability of transition (c) is negligible with respect to (b), Fig. 1, since both of these transitions must eventually result in the radiation of 5890A. In order to test the validity of this assumption the calculations carried out by Prokofjew[3] were extended to give an estimate of the relative probabilities of transitions (b) and (c) and it is found that this ratio is large enough (of the order of 50 to 1) that radiation due to transition (c) may be neglected.

In this investigation the effect of the addition of foreign gases upon the fluorescence of sodium, excited by 3303A, is studied. In order to carry out the investigation quantitatively it was found necessary to design a new type of arc of greater intensity and stability of operation than any of those thus far described in the literature.

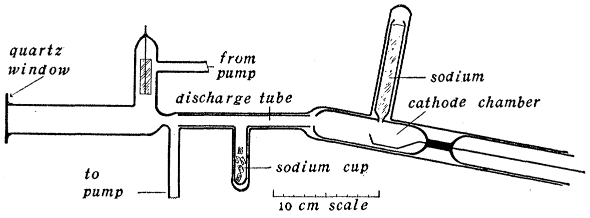

Fig. 2.

Figure 2, drawn to scale, gives the design of the arc. The quartz window and removable cathode are both sealed to the Pyrex with Dennison sealing wax. The electrical leads through the Pyrex are of tungsten and the anode is a cylinder of sheet nickel sealed to the tungsten wire with German silver. The cathode is of metallic sodium held in place by the cathode chamber, as shown in the diagram, with the electrical contact made directly to the tungsten wire.

The cathode chamber is made removable to facilitate refilling in case this becomes necessary. The sodium is introduced by placing a tube containing purified metal in the charging tube, as shown in the diagram, with one constricted end inserted in the small hole in the cathode chamber, sealing off the end of the charging tube, evacuating, and then heating the charging tube until the sodium melts and runs down. The discharge tube and sodium cup are placed inside a larger tube of the same shape to prevent the hot sodium from coming in contact with the wall which must remain vacuum tight. The sodium in the cup can be introduced in small tubes which are cut short enough to allow them to be inserted through the front of the arc before the quartz window is attached. The cup and discharge tube are equipped with heaters and temperature controls, although the heat produced by the discharge is generally enough to maintain a sufficiently high temperature in the discharge tube. Argon is circulated through the arc as indicated, by means of a mercury pump with two liquid air traps filled with beads to remove the mercury vapor from the gas stream.

The sodium used is purified by first heating it for several hours, under vacuum, in such a way that it continually distills on to the sides of the flask and runs down again. This is done to expel occluded gases, especially hydrogen. When a very high vacuum is obtained the sodium is distilled through a side tube of large diameter and collected in tubes.

This arc is similar to that designed by Christensen and Rollefson[5] which we shall hereafter refer to as the "old type," but differs from it in several important respects. In the old type the cathode was heated and used as a part of the light source. In the new type it is not heated but is allowed to cool as much as possible and is not used as a part of the light source. The entire radiation, with appreciable intensity, is produced in the discharge tube in which the vapor pressure of sodium is controlled by the temperature of the sodium cup, the temperature of the discharge tube being always kept slightly higher. One advantage of this is the more accurate control of the vapor pressure of sodium which it affords, this being one of the chief factors involved in producing a discharge with constant intensity.

It is also found that the cool cathode eliminates a large degree of uncertainty of operation which was experienced with the old type. The trouble was undoubtedly connected with some sort of surface phenomenon, for it was always observed that whenever the "active point," usually visible on the surface of the cathode, was replaced by a diffused glow over the entire surface, the current dropped to a very small value with a corresponding decrease in intensity. This behavior was usually followed by complete failure. It was often found, however, that after allowing the cathode to cool, the arc could again be started at its normal current and also that heating the cathode to a higher temperature would result in breaking the discharge or reducing the current. It was further found that, whenever the $H\alpha$ line was present in the spectrum of the discharge, almost certain failure of the arc occurred. In view of this fact a tube of hot copper oxide was placed in the stream of circulating gas which reacted with the hydrogen changing it to water vapor which was removed in the same liquid air traps used to remove mercury vapor. This, of course, could remove only that portion of the hydrogen, present or produced in the back of the arc, which diffused into the circulating stream.

These difficulties are all eliminated in the new type of arc. The entire surface of the cathode chamber is usually found covered with sodium and the "active point" is seen to travel in a very devious path all over the surface. Even when the $H\alpha$ line is present in the spectrum of the discharge in appreciable amounts, this arc operates quite satisfactorily. In the old type whenever the cathode chamber was removed, after a few hours operation, it was always

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[5] Christensen and Rollefson, Phys. Rev. **34**, 1154 (1929).

found to be cracked and had to be replaced. In the new type the cathode chamber does not crack and can be used again if refilling becomes necessary.

When the vapor pressure of sodium in the discharge tube is too low the arc will "flicker" but as the vapor pressure is increased the flickering ceases and a very steady discharge is maintained. As the vapor pressure is still further increased the intensity of the 3303A line gradually decreases. The optimum pressure is very easily obtained by increasing the temperature of the cup until the flickering just ceases.

The arc operates quite satisfactorily with about 0.5 cm of argon circulating through it. At lower pressures of argon the sodium diffuses out of the discharge tube quite rapidly, while increasing the pressure decreases the intensity of the 3303A line due to the quenching effect.

One of these arcs has been operated with 220 volts direct current at 2.5 amperes for about 150 hours and it seems in as good a condition as when new. This arc was operated with as low as 90 volts but some difficulty in starting it was encountered without the higher potential. A high frequency spark was used to start the arc.

This current of 2.5 amperes is by no means the maximum possible. By using less resistence in series with the arc the current can be increased to several times this value and one of these arcs was operated at 6 amperes for a period of one-half hour with perfectly satisfactory results.

For studying the fluorescence the apparatus assembly was identical with that described by Christensen and Rollefson with the addition of a small-diameter quartz tube, with a graded seal to Pyrex, leading from the fluorescence tube to the apparatus used to introduce varying pressures of foreign gases. The mean free path of sodium atoms in the pure vapor is so large, at the temperatures used, that the leak of sodium vapor through this tube is negligible. The foreign gas was always introduced while the fluorescence tube was cold, in order to prevent sodium vapor from being swept to the front and condensed on the window. It was found that addition of the foreign gases increased the necessary temperature of the hot air stream used to prevent condensation of sodium on the windows. An air stream of about 400°C was used with the fluorescence tube at 180–200°C. It was also found that with the air stream at this temperature, the temperature of the fluorescence tube necessary to cause "browning" was very much greater than when the air stream was kept at 280°C. This indicates that "browning" is preceded by condensation of sodium.

The assembly was constantly checked for stray light by making exposures for long periods with the fluorescence tube cold.

The helium gas used was passed through charcoal at both liquid air and liquid hydrogen temperatures. The nitrogen was passed through a tower filled with copper turnings and ammonium hydroxide to remove oxygen and then through a liquid air trap. The hydrogen was made electrolytically and was passed over hot copper to remove oxygen and then through charcoal at liquid air temperature.

The Wratten and Wainright panchromatic plate was used and a standard developer and development procedure was adopted in order that blackenings on different plates might be compared. All the plates used were from the same box. All the photographs used to plot any one curve were taken on the same plate. The exposures of the fluorescence excited by 3303A radiation were taken over periods of one-half hour, one hour, two hours and three hours. The longer exposures were used in order to get blackenings of a density most accurately determinable, when the intensity was diminished by the addition of foreign gases. Photographs were also taken of the fluorescence when excited by *D* light. When a screen of approximately 10 percent transmission was inserted in the exciting beam, exposures of 10 seconds, 20 seconds, 40 seconds and 80 seconds gave satisfactory blackenings.

The photographic blackening densities were determined with a Zeiss microphotometer. All the photographs of the fluorescence and those taken to obtain the blackening—intensity calibration curves were photometered with the same adjustments of the instrument, and the readings were recorded on the same arbitrary scale. The blackening of any photograph could then be translated into intensity in terms of percent of an arbitrary standard.

The calibration curves were obtained with a direct current helium discharge operated by a 600 volt battery assembly at a current of 0.36 milliamperes in the case of the longer exposures and 0.8 milliamperes for the shorter exposures. The current was easily controlled to within 2 percent by gradually decreasing the resistance in series as the operating voltage of the battery decreased.

This discharge has strong lines at 5875A and 3187A as compared to 5890A and 3303A in the sodium fluorescence. A consideration of Harrison's work in spectral photometry, indicates that the use of these lines for calibration purposes is justified within a limit of 2 percent accuracy. For the longer-exposure calibrations a filter of $CrCl_3$ solution in a quartz vessel was placed between the discharge and the spectrograph. This absorbs a certain percentage of the 5875A radiation which is the more intense of the two and by varying the concentration of the solution the blackening produced by the two lines can be made approximately equal. This makes it possible to determine the calibration curves for both wave-lengths at the same time. For the calibration curves used with *D*-light excitation the $CrCl_3$ filter was not inserted since only the intensity of the 5875A line was needed.

Screens, calibrated for transmission with a thermopile, were used to reduce the intensity by a known fraction. The screens were kept moving and when two screens were used simultaneously they were moved in opposite directions at all times.

Photographs were obtained of the fluorescence excited by 3303A radiation and by *D* light with varying pressures of helium, nitrogen and hydrogen in the fluorescence tube and the resulting intensity curves are given below.

In Fig. 3, which shows the effect of helium on the fluorescence, curve *A* gives the variation in intensity of the 3303A line, the dots represent intensities with the fluorescent cone at a depth of 3 mm from the observer's side of the fluorescence vessel and the crosses are for a depth of 10 mm, the circles represent a theoretical quenching curve. Curve *B* gives the intensity of the "*D*" light when excited by 3303A the fluorescent cone being at a depth of 3 mm, curve *C* gives the intensity of "*D*" light with the cone at a depth of 10 mm. Curve *D* gives the intensity of *D* light excited by *D* light. In each case the intensities are in terms of the intensity with no helium present.

From the energy-level diagram for sodium, Fig. 1, it may be seen that the decrease in intensity of the 3303A line may be explained in two different ways. It may be due to transfers, by collisions of the second kind, of atoms in the 3*P* state to any one of the other four states designated. In other words it may be purely a quenching phenomenon. Also, it may be due to a change in the relative transition probabilities, effected by the presence of the helium, in favor of transitions "*b*" or "*c*". A combination of these two effects is also possible.

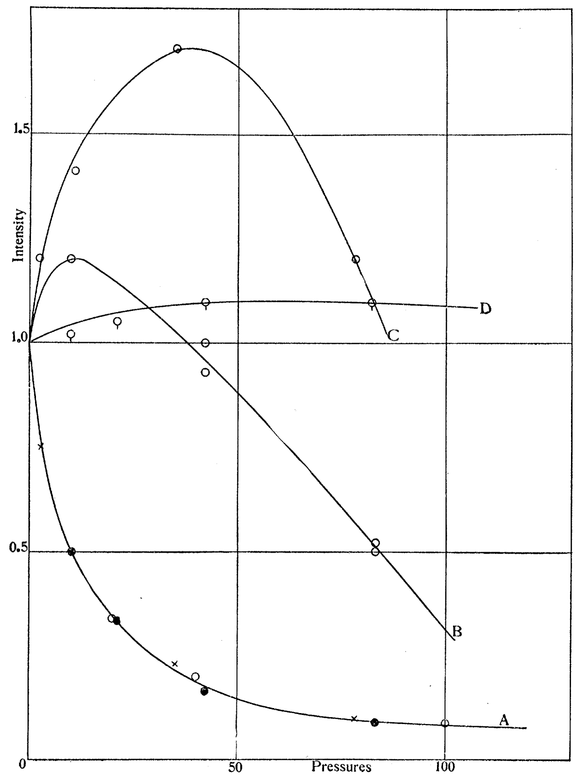

Fig. 3.

If the collisional transfers occur to either the 3*D*, 2*S* or 2*P* state the effect upon the relative intensities of the 3303A and 5890A radiation is exactly the same as that produced by a change in the relative transition probabilities. However, the dependence of each of these effects upon the pressure of foreign gas may serve as a method of distinguishing them.

A theoretical quenching curve is determined by the expression for the fractional decrease in intensity

$$100 - I = \tau/(\tau + T),$$

where τ is the mean life of the excited atom, T is the mean time between effective collisions and I is the percent of the intensity of the unquenched radiation. At the pressure designated by $p_{1/2}$ at which the intensity has been reduced 50 percent it is evident that τ is equal to T, and we then have the following relations

$$T = k/p; \quad \tau = k/p_{1/2}$$

where p is the pressure at constant temperature and k is a proportionality factor. We may then write

$$100 - I = \frac{k/p_{1/2}}{k/p_{1/2} + k/p} = \frac{1}{1 + p_{1/2}/p}\,. \tag{1}$$

Replacing $p_{1/2}$ in Eq. (1) by the value obtained from any quenching curve gives the theoretical formula for that curve.

The small circles near curve A, Fig. 3, represent points on a theoretical quenching curve with the value for $p_{1/2}$ taken from curve A. The excellent agreement between the observed and calculated curves is evidence in favor of the supposition that the decrease in intensity of the 3303A radiation is due to a collisional effect and that the presence of helium has no apparent effect upon the relative transition probabilities.

Any effect upon the transition probability which depends upon the interaction of the excited sodium atom and a foreign gas molecule, at the instant of radiation, such as the effect of the electrostatic field, would be directly proportional to the pressure and independent of the life period of the excited atom since only its position at the instant of radiation is of importance. This straight-line relation might be slightly altered by the second order effect of multiple interaction. If the time required for the act of radiation is finite and if at any time during the act, interaction with a foreign gas molecule is effective in changing the transition probability the change in intensity will take the form of a quenching curve, but the value of τ will be different from that in the true quenching formula and the two effects cannot be superimposed. The two phenomena are indistinguishable only in case the effect of the foreign gas molecule is such that at any time during the normal life period of the excited atom, that interaction occurs, it may be caused to radiate or be so affected that when it does radiate its relative transition probabilities will have been changed. In case successive collisions are effective in changing the transition probability, the intensity variation will depend upon some higher power of the pressure.

Curve D, Fig. 3, gives the observed intensity for D light when excited by D light, and when compared with the data obtained by Mannkopff[6] using a resonance lamp for excitation it is evident that a considerable amount of increased absorption has occurred due to the pressure broadening of the absorption line. This is to be expected since the center of the incident D line is

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[6] Mannkopff, Zeits.f. Physik **36**, 315 (1926).

very markedly absorbed and at the point of observation the excitation is due mainly to the remaining broadened portion. Consequently, the intensity is greatly affected by any broadening of the absorption line. In the case of the 3303A excitation, since the amount of absorption is very small there is still sufficient intensity in the center of the incident line at the point of observation to render the broadening effect negligible. This is verified by the close agreement between curve *A* and its theoretical quenching curve.

Curves *B* and *C*, Fig. 3, which give the intensity variation of *D* light when excited by 3303A, show the resultant of two effects—the increase in intensity due to collisional transfer of atoms from the *3P* to the *3D*, *2S* or *2P* states, and the decrease in intensity due to complete quenching of atoms in any one of these states.

Boeckner[7] found that the probability of caesium atoms in the *4P* state being transferred by collision to the *5D* state was approximately twenty times that of being transferred to the *3S* state. The energy difference in the first case is 0.043 volts and in the second case 0.18 volts, a factor of approximately 4. By analogy it seems certain that most of the collisional transfers from the *3P* state of sodium will be to the *3D* rather than to the *2S* state, since the ratio of the energies involved is almost identical with that in the caesium atom, as are also the important quantum numbers. It may certainly be assumed that the number of atoms transferred to the *1S* state, an energy difference of approximately 30 times as great as that between the *3P* and *3D* states, will be negligible. The increase in intensity due to the collisional transfers is not solely a matter of increasing the number of atoms radiating *D* light but also involves a decrease in the absorption because of an increased "Doppler width" of the fluorescence light. If it were not for the latter effect curves *B* and *C* should be identical, however, with this change in absorption the observed rise in intensity of the *D* light will be greater for the greater depths. The two curves will coincide when enough collisions occur between the time the atom is changed from the 3^2P state by a collision and the time at which the quantum of "*D*" light is emitted to restore the atoms to the normal distribution of velocities. From the results we have obtained it is obvious that this does not occur except at pressures well in excess of 100 mm of helium which means that the fast moving excited sodium atoms retain their high speeds for a large number of collisions. The fact that at high pressures the "*D*" light intensity drops below that which would be calculated from Mannkopff's data on quenching indicates that under these conditions some quenching to the 1^2S state occurs.

Figure 4 gives the results obtained when nitrogen and hydrogen were introduced into the fluorescence tube. In each case only the data for the 3303A line are plotted as the curves for the "*D*" light did not differ from these to any marked degree. The absence of any increase in the "*D*" light intensity such as was found with helium is taken to indicate that for these gases the quenching process involves returning the sodium atom to the 1^2S state. On the nitrogen

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[7] Boeckner, Bur. Standards J. Res. 5, 13 (1930).

curve the dots represent the experimental points and the circles give the theoretical form for the quenching curve. From the close agreement between the two sets of points we may conclude that nitrogen has no pronounced effect upon the transition probabilities in the 3^2P state of sodium.

The data for the hydrogen curve are subject to some uncertainty due to the fact that the presence of hydrogen seems to accelerate the reaction between sodium and quartz causing a change in the transmission of 3303A through the windows. However, the observed points follow a theoretical quenching curve so well that it may be said that hydrogen has no effect on the transition probabilities.

The most probable source of error in the measurements is in the variation in the intensity of the arc and in the temperature controls throughout the apparatus. This was checked by taking a series of consecutive photographs of the fluorescence, as used in the experiments. These were taken over a period of 4 hours and a deviation of not greater than 10 percent in the intensity was observed. The accuracy of the photometry was well within this limit. It seems, therefore, that an error of not greater than 10 percent is to be expected in the measurements.

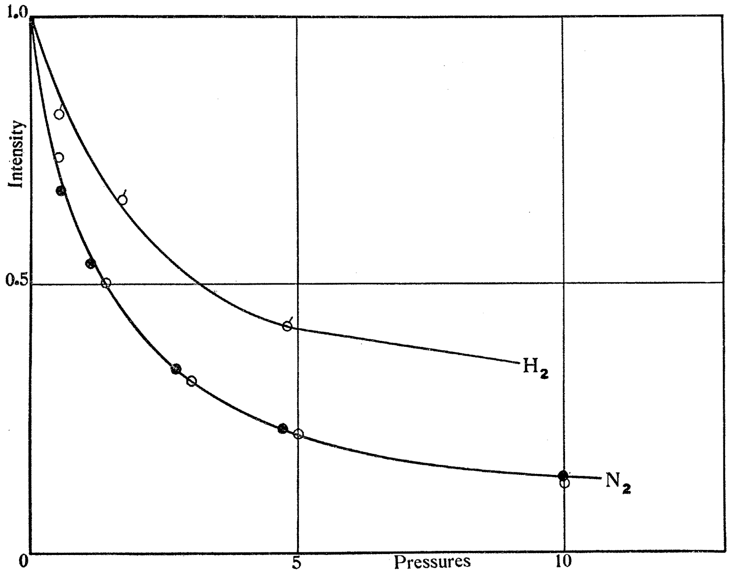

Fig. 4.

The results of this investigation demonstrate that there is no apparent effect upon the transition probabilities in the $3P$ state of sodium when the excited atoms are subjected to the presence of an inert gas. Therefore, some other phenomenon must be responsible for the difference between the intensity ratio obtained by Weiss and that obtained by Christensen and Rollefson.

A separation of the $3P$ level into two or more levels having different transition probabilities and different populations might be assumed as a possible explanation. This separation may or may not be the nuclear hyperfine structure. Let it be supposed that in the pure fluorescence the number of collisions during the mean life capable of transferring excited atoms from one of these states to the other is negligibly small. The radiation observed might be supposed to come largely from a state in which the ratio of the probabilities of transitions (b):(a) is small, with a smaller amount coming from a state in which this ratio is much higher. The high pressure of inert gas present in the arc as used by Weiss, due to transfers by collisions of the second kind, would tend to make the population in both states equal. It is then evident that the ratio of the intensities of these two transitions would be immediately increased.

This same effect, however, should be observed when inert gas is introduced into a fluorescence tube. It should appear in the investigation presented here as a decrease in the intensity of the 3303A radiation on the addition of helium. An obvious assumption would be that at least every kinetic theory collision would be effective in transferring atoms between states differing by so small an amount of energy as must be assumed between such states as those being considered here. At 10 mm pressure of helium, sodium atoms in the $2P$ state undergo on the average 4.5 kinetic theory collisions during the mean life of the excited atom. The figure for the $3P$ state should be at least as great. It is therefore to be expected that equilibrium between states within the $3P$ state should be reached at this pressure. A change in the ratio of the probabilities of transitions (b) and (a) from 1.7:1 to a ratio of 25:1 would result in a 90 percent decrease in the intensity of the 3303A radiation. From curve *A*, Fig. 3, it may be seen that at 10 mm pressure the intensity of the 3303A radiation has been decreased only 50 percent. This seems to be conclusive evidence that the explanation presented above is not valid.

The difference in the method of excitation has been suggested as a possible explanation, but if this difference is postulated as a method of putting atoms into different states within the $3P$ state, the argument is subject to the same objection presented in the preceding paragraph. In the arc there should be complete equilibrium and in the fluorescence equilibrium should be quickly established on the addition of inert gas, but this is found to be not the case. If it is assumed that the method of excitation causes some permanent change in the $3P$ state as an entity, the above objection no longer holds.

In general it may be said with some degree of certainty that the experimental evidence obtained in this investigation presents a very serious objection to any explanation of this disagreement in intensity ratios which depends upon a difference in transition probabilities of states within the $3P$ state.

Another possible explanation suggests itself when one makes an assumption concerning the actual mechanism of radiation of which so little is known. It seems not impossible to imagine that this mechanism is such that when more than one transition is possible, on the average that transition of greatest probability will occur in the shortest length of time; or, in other words, that the life period of the excited atom varies inversely as the transition probability of the radiation which occurs. This may be stated in another way: that the chance of that radiation occurring which has the least probability increases with increasing life of the excited atom. It is doubtful that there is as yet any experimental evidence which can conclusively prove or disprove this assumption.

If this assumption is made, however, the explanation sought is immediately forthcoming. The measurements of Weiss were made by observing the radiation from sodium atoms in the *3P* state in the presence of argon at a comparatively high pressure. It is then to be expected that something over 90 percent of the atoms in the *3P* state were transferred to the *3D* state before they could radiate and the relative intensities measured were of the radiations emitted by only those atoms which had survived this collision process. The number of collisions increases with increasing life period, consequently more of the atoms with shorter life periods than of those with longer life periods will survive the collision process. The relative intensities of the radiations will then change in favor of that one having the shorter life period; or on the basis of the assumption suggested above, the relative intensities would change in favor of the transition with greatest probability. In the case of the *3P* state of sodium it would then be expected that the ratio of the intensities of the transitions (b): (a), Fig. 1 would be greater in the presence of a high pressure of argon than in the pure fluorescence, since transition (b) is the one of greatest probability.

The assumption suggested above is at least partially vindicated by the work of Randall[8] and of Richter[9] who found independently and by entirely different methods that the life periods of the atoms in the 2^3S_1 state of mercury appear approximately four times as great when the 5461A radiation is observed as when either the 4358 or 4047 line is observed. As an explanation of this it was suggested that the life periods and transition probabilities might be different for each hyperfine structure level, and Frisch and Pringsheim[10] attempted to demonstrate this by exciting mercury atoms to the 2^3S_1 state by different methods but found no variation in the relative intensity.

Mrozowski[11] gives some theoretical evidence against the possibility of any influence of nuclear moments on the life period but suggests that there is some sort of separation of the 2^3S_1 state into states with different life periods and different transition probabilities.

In the investigation carried out by Randall no complexity was observed in the constant k which was used in the formula C^{-kt} to describe the falling off of intensity with time after excitation. This indicates that all of the atoms radiating a particular wave-length had the same life period, and therefore probably existed in the same state. This prerequisite would be complied with if all the radiation was assumed to come from the same level but from atoms whose life periods depended upon the wave-length radiated.

Another very serious objection to any explanation of this difference in life

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[8] Randall, Phys. Rev. **35**, 1161 (1930).

[9] Richter, Ann. d. Physik **7**, 293 (1930).

[10] Frisch and Pringsheim, Zeits. f. Physik **67**, 169 (1930).

[11] Mrozowski, Zeits. f. Physik **68**, 278 (1931).

periods which depends upon a multiplicity of the 2^3S_1 state is encountered when we consider the experiments which have been performed demonstrating the extremely large efficiencies or collisional radii for processes involving such small energy differences as there must be between such states.[12] It seems almost necessary to assume that in the experiments performed by Randall complete equilibrium between the populations of such states must necessarily have been established, and if this were the case a difference in life periods could not have been measured. It is also impossible that there could have been only a partial equilibrium since Randall found that varying the pressure had no effect upon the life periods measured. It seems therefore almost necessary to assume that either the life periods of atoms in any excited state may depend upon the wave-length radiated or else that there are states within the one state with different life periods and transition probabilities between which strong argument in favor of the explanation based upon a change in relative intensity due to quenching, which is presented above concerning the disagreement in the intensity ratios in the $3P$ state of sodium.

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[12] Experiments by Wood and Mohler, Phys. Rev. **11,** 70 (1918), have shown that when Na vapor is excited by a single D line and the temperature of the fluorescence is above 220°C, both D_1 and D_2 appear in the fluorescence due to transfers by collision from one member of the doublet P state to the other. Datta, Zeits. f. Physik **37,** 625 (1926), in experiments on the depolarization in the resonance fluorescence of sodium finds an effective radius of approximately 10^{-4} cm, or approximately ten thousand times that of the normal kinetic theory radius.