PHOTOELECTRIC EMISSION AS A FUNCTION OF COMPOSITION IN SODIUM-POTASSIUM ALLOYS

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Abstract

The entire series of alloys of sodium and potassium have been investigated with respect to the relative values of the photoelectric currents produced by light polarized with the electric vector in and at right angles to the plane of incidence. The pure metals when molten exhibit values below three for the ratio of the two emissions; the alloys show *three maxima* at compositions approximately 20, 50, and 90 atomic percent of sodium, with values from 10 to 30 for the ratio; the minima between show low values approximating those for the pure metals. The maxima and minima of the ratio of emissions are due to complicated variations in magnitude of the two emissions compared.

ELSTER and Geitel discovered that the photoelectric emission from the liquid equimolecular alloy of sodium and potassium is greatly altered in amount when the plane of polarization of the (obliquely incident) light is varied.[1] They do not appear to have investigated alloys of other proportions than those of the equimolecular one. Pohl and Pringsheim,[2] who studied the photoelectric properties of this alloy, as well as of the pure alkali metals separately, worked under the belief that the high ratio of the emissions occurring when the light is polarized with the electric vector first in, then perpendicular to the plane of incidence (*selective* and *normal* effects) was a characteristic of the pure metals as well. Subsequent work[3] has however shown that pure sodium and potassium, in the liquid form, do not exhibit (at least in the visible spectrum) the high ratio effect found in the equimolecular alloy. It becomes therefore of interest to learn how the photoelectric properties, particularly the ratio of emissions defined above, vary with the relative proportions of sodium and potassium in the alloy.

In order to investigate this question, we made up a series of photoelectric cells of the form shown in Fig. 1. These were simple spherical bulbs made of Pyrex glass and provided with electrodes. An auxiliary side bulb was attached, into which the alloy was introduced first, by distillation, and from which it was poured into the main bulb, — a procedure found advisable for removing any traces of floating impurity.

[1] Elster and Geitel, Ann. d. Physik **LII**, p. 433 (1894).

[2] Pohl and Pringsheim, "Die Lichtelektrischen Ersheinungen" Vieweg (1914).

The alloys were prepared in the distilling system by the following method. Pure sodium and potassium were first distilled in vacuo separately into long pyrex tubes (of about 1 cm diameter). From these tubes, pieces were broken off as nearly as possible of the proper lengths to give the alloy desired. These pieces, after weighing, were introduced into a multiple bulb distilling system attached to the photoelectric cell. The alkali metals were then melted and completely distilled over in vacuo, following the general method and precautions described in earlier papers.[3] After the distilling system was sealed off, the pieces of glass tube which had contained the alkali metals were weighed, and the difference in weight before and after gave the amounts

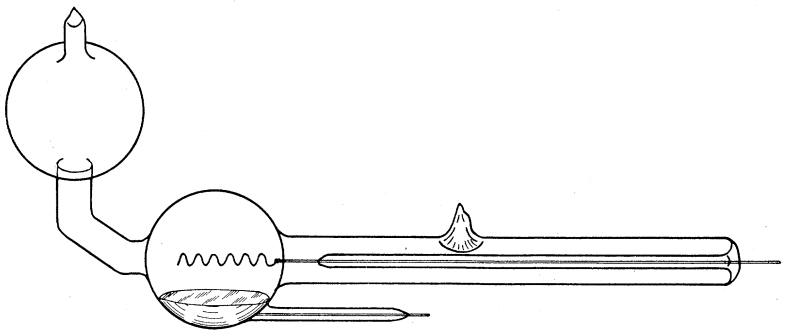

Fig. 1. Type of photoelectric cell used for studying emission characteristics of Na-K alloys.

of alkali metal. Some error is introduced through the crust of oxide which forms at the ends of the columns of alkali metal in the glass tubes. This error can be made relatively small by using tubes of generous length.

Photoelectric currents were excited by the total light of a helical-coil tungsten filament, incident at an angle of 60° after passing through a nicol prism and a lens which focussed an image of the filament on the alloy surface. The cells were operated with 120 volts of applied potential, and the currents were measured on a high-sensibility d'Arsonval galvanometer.

Before giving the results of the measurements it is desirable to discuss some details with regard to the alloys. First of all, it is of extreme importance that the two metals used be pure. The criterion for purity which we have found most useful is really an outcome of this study, and its statement here partially anticipates the conclusion from the

[3] Ives and Johnsrud, Astrophys. J. **LX**, 4, p. 231 (Nov. 1924).

work. The criterion is this: *the ratio of emission defined above for illumination by light incident at 60°, shall be not more than 2 or 3 to 1* for the pure metals when liquid just above their melting points. A very small admixture of either metal with the other greatly increases this ratio. Also it appears probable that other materials than the alkali metals, when present as impurity, may raise the ratio. All our samples of sodium and potassium, after the preliminary distillation, and before being used for the preparation of alloys, were tested by this criterion in a trial cell. It was found that some of the

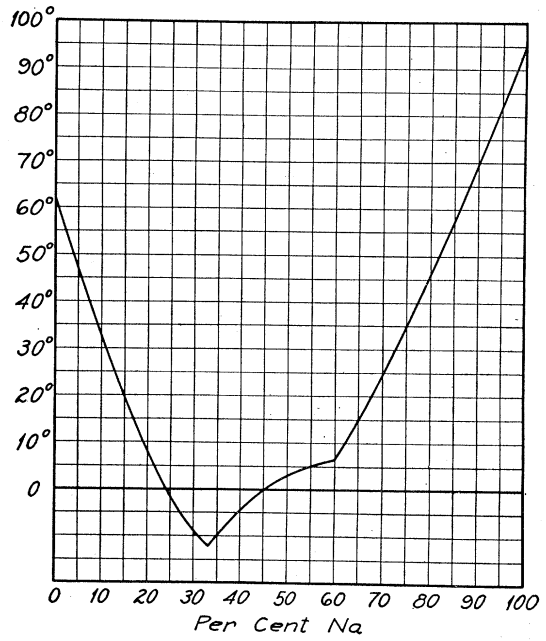

Fig. 2. Melting points of Na-K alloys.

"pure" sodium and potassium obtained from chemical-supply firms fails to meet this test. The greater part of our work has been done with metals from Mallinckrodt, which have uniformly given a low value for the ratio in question.

The physical properties of the Na-K series have already been rather thoroughly studied. The relationship between melting point and composition is given by Kurnakow and Puschin,[4] whose results are shown in Fig. 2, here reproduced for reference. It will be noted that all alloys in the range from 15 to 70 atomic percent of sodium are liquid at room

[4] Kurnakow and Puschin, Zeits. Anorg. Chem. **30**, p. 109 (1902).

temperatures. Since for our purposes the surface must be specular, the alloys in this range are suitable for study at room temperature. The alloys outside this range were warmed just sufficiently to melt them. Through the middle of the range of alloys liquid at room temperatures the liquid appears perfectly homogeneous, not unlike mercury. The alloys on the borderline between the liquid and solid states at room temperatures frequently exhibit a surface structure apparently consisting of floating crystalline plates or of liquid pools separated by projecting thin crystal walls. These crystalline formations sometimes persist as the alloy is cooled, and can frequently be observed in pure slowly-cooled solid sodium and potassium, thus affording nearly specular surfaces suitable for optical measurement.

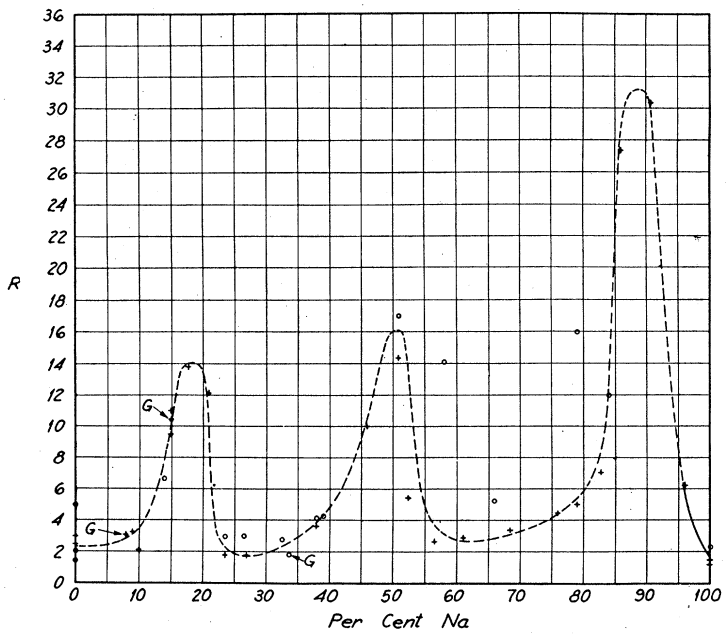

Fig. 3. Ratio of photoelectric emissions for excitation by obliquely incident light polarized in two directions ("selective" and "normal") as a function of atomic percentage of Na in Na-K alloy.

The first series of observations here reported are those made on approximately forty cells of the type of Fig. 1. The results are shown in Fig. 3, where the abscissas represent alloy compositions in atomic percent, the ordinates represent the ratio:

$$R = \frac{\text{emission with electric vector in the plane of incidence}}{\text{emission with electric vector perpendicular to the plane of incidence}}.$$

The outstanding fact is the occurrence of *three maxima*, two close to the ends of the diagram, and one at the middle, corresponding to the equimolecular alloy. Every cell made up is represented in the figure, without regard to the fact that in the earlier cells the quantities of the two metals used were too small to enable us to ascertain the relative proportions as accurately as was later done, resulting in a greater scattering of results and consequent blunting of the maxima. The observations designated by crosses form the group made last, when the technique was most completely developed, and should be given the greatest weight. They indicate that the maxima are quite sharp. Several observations, marked *G*, were made on cells in which the vacuum was imperfect, as shown by the characteristic rapid increase

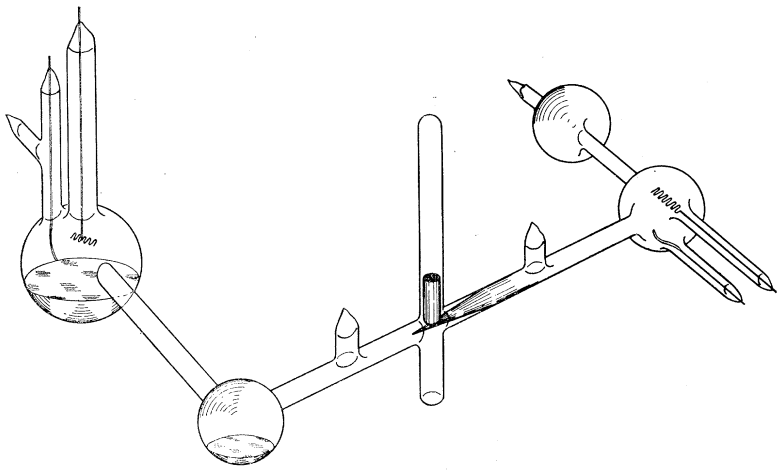

Fig. 4. Special cell used to study complete series of Na-K alloys by successive additions of K (from right-hand bulbs) to Na (in left-hand bulb).

of current with voltage, or by the occurrence of a glow discharge when tested with a spark coil. It will be noted that these cells fall in their proper places on the curve, indicating that the emission ratio R is not affected by the presence of gas.[5]

The data of Fig. 2 show merely the *ratios* of emissions. It is of interest to know how the two emissions in question vary individually.

[5] Fleischer and Dember in Zeits. f. Tech. Phys. **3,** 1926, p. 133, report experiments on potassium in which the emission characteristics of a sealed cell changed with time. The title of their article states that the photoelectric properties are studied with regard to their dependence on gas content. Actually no measurements were made of gas pressure nor was any evidence given that the gas content varied. In the light of our work, it appears to us more probable that the change occurring with time was in the crystalline structure of the surface.

This information cannot be deduced from the measurements on separate cells, each containing different alloys, because of differences in the total emission due to unavoidable variations of conditions occurring in their preparation. In order to determine the emissions in absolute measure, it appeared necessary to construct a cell in which the composition of the alloy could be altered progressively. For this purpose, a double cell was made, as shown in Fig. 4; the two sections were separated from each other by a thin cone-shaped glass diaphragm which could be broken by a falling slug of iron after the two cells had been separately filled with alkali metal and exhausted. Molten metal from one cell could then be allowed to flow by small increments into the other. In order to get an approximate measure of the proportions of the alkali metals present as the mixture proceeded, the bulb selected for the mixing chamber was calibrated beforehand by putting in known volumes of mercury and measuring the dimensions of the mercury pool with a cathetometer. If the meniscus of mercury were the same as that of the Na-K alloys this would afford a reasonably exact measure. Actually the alloys near the sodium end (which were the first produced, potassium being added to an initial small globule of sodium) differ in shape of meniscus quite markedly from mercury, so that the volume measurements were not very satisfactory near the sodium end of the series, and must be taken as merely approximate. (Were the experiment to be repeated, the alloy pool would be photographed in profile and plan, and the volume determined by area measurements of the photographs). The measurements however do show the progressive change in composition sufficiently for the immediate purpose.

The results of this experiment are shown in Figs. 5 and 6. Considering first the behavior of the ratios of emission under the two conditions of polarization (Fig. 5) it appears that the three maxima obtained with the forty individual cells are confirmed. The maxima are not however so sharp, the central maximum is doubled, and is relatively higher and wider, so that the neighboring minima are not so low as in the individual cells. These differences between the behavior of the alloys in separate cells and the progressive mixture are, we believe, to be ascribed to the fact that with the separate cells there was ample time for the alloys to attain equilibrium, while with the series in a single cell the measurements were made immediately after each mixture, and often only a few minutes elapsed before the next step of the series was undertaken.

Considering next the behavior of the two photoelectric currents separately (Fig. 6) we see that the maxima and minima of the ratio are associated with a very complicated course of the two constituent

emissions. Thus taking the "normal" current case "$E \perp$" this exhibits a minimum at approximately 12 atomic percent Na, and a maximum at 25 atomic percent. The maxima and minima in the ratio at 18 and 30 atomic percent are almost entirely due to these variations in

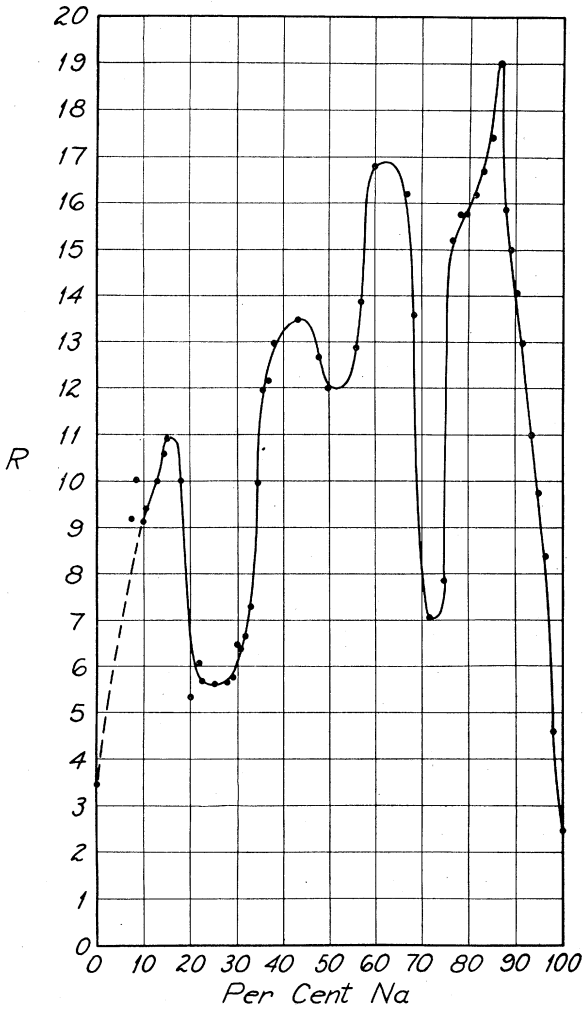

Fig. 5. Ratio of "selective" to "normal" emissions as obtained from series of alloys mixed in cell shown in Fig. 4.

the "normal" current, since the "selective" effect merely shows a practically uniform increase through this region. Toward the other end of the series however, the condition is reversed. While the "normal"

emission ($E \perp$) decreases slowly, the "selective" emission ($E \parallel$) interrupts its gradual rise by a sharp drop and subsequent rise, which accounts for the minimum in the ratio in the neighborhood of 70 atomic percent. It is evident from Fig. 6 that the phenomena are

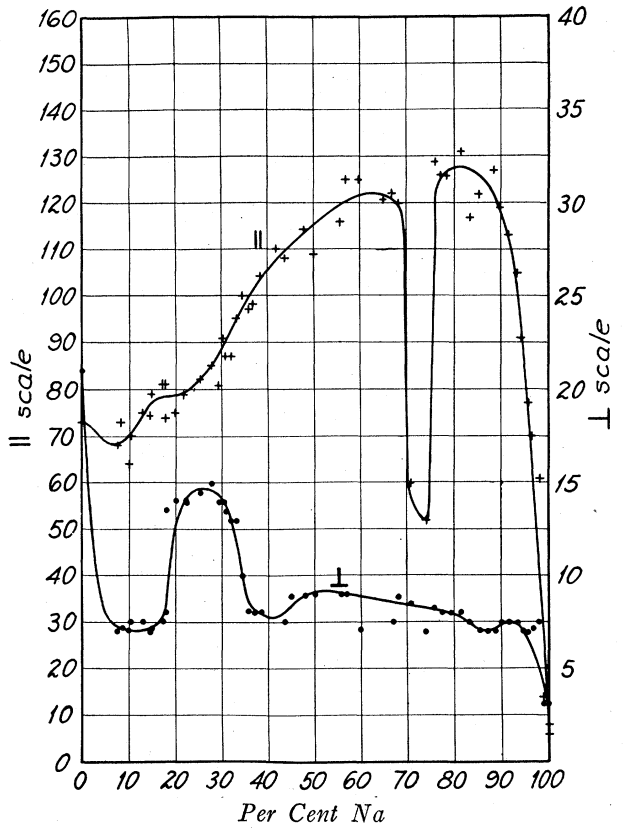

Fig. 6. Variation of "normal" ($\perp$) and "selective" ($\parallel$) emissions as function of Na-K composition, as obtained in cell shown in Figure 4.

quite complex; to obtain complete information, it will be necessary to study the emission with spectrally resolved light. This will be undertaken at an early date.

Discussion

In previous papers, it has been suggested that the great difference in photoelectric emission which occurs in certain cases when the plane of polarization of the exciting light is varied, is to be attributed to a regular orientation of the surface atoms or molecules. The results

of the present study may be interpreted in the same way if we consider the sodium and potassium atoms as forming a series of atomic groups, as the relative proportions of the metals vary. Certain of these groups may be pictured as consisting of chains or other structures which will tend to become oriented in definite ways at the liquid surfaces, and to respond differently according to the direction of the electric vector with respect to the surface. The coincidence of the central maximum with the composition KNa, supposed to be a metallic compound, is suggestive. There appears however to be no other correlation with either integral atomic proportions, or with other physical properties as indicated by the melting point data. A possible working hypothesis is that the maxima close to the two ends of the series are to be ascribed to surface layers of unit atomic thickness of potassium or sodium. Further light may be obtained on these questions by studying the distribution of response through the spectrum.

In a previous study of a sodium-potassium alloy,[3] support was found for the hypothesis of orientation of the surface atoms or molecules by the fact that the ratio of emissions was greatly reduced in value when the alloy was heated. This observation has been completely confirmed in the present work by numerous observations on alloys all through the series, which however need not be shown, since they are adequately represented by the data shown in the earlier paper. The evidence for the existence of orientations of atoms at the surface has been supplemented in the present work by the actual observation of crystalline planes on the surface of semi-molten alloys, as already mentioned. The selective-normal ratio of emissions from these crystalline surfaces is in all cases higher than from the same material when completely melted. Further evidence of the same sort is obtained from the observation that pure sodium may solidify with flat specular areas, and these, unlike the previously observed specular solid potassium,[3] and unlike molten sodium, show relatively high ratios (7 to 8) for the selective-normal ratio. These high values rapidly drop as the temperature of the solid sodium is raised, approaching the molten value (2-3) continuously. The high ratios found in smooth solid sodium increase as the cell stands, suggesting an increasing crystalline character of the surface.

It may be noted that the conclusion drawn in an earlier paper[3] that sodium-potassium alloy is the only one of the alkali metal alloys which has a high selective-normal ratio may be subject to revision in the light of the new results on Na-K allloy It is possible that alloys

of the other alkali metals, in different proportions than those thus far studied will show high values for this ratio.[6]

We desire in conclusion to acknowledge our indebtedness to Mr.A. L. Johnsrud for his aid in the volume measurements used to determine the alloys compositions.

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[6] Another factor contributing to the occurrence of high ratios has been found since the work here described was completed. This is a failure of the proportionality between photoelectric current and illumination for the "normal" emission. This will be treated in a later paper.