ANALYSIS OF POSITIVE IONS EMITTED BY A NEW SOURCE

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Abstract

Certain iron oxide crystals containing about one percent of some alkali metal or alkaline earth have been developed by the Fixed Nitrogen Research Laboratory for use as catalysts in the synthesis of ammonia. It has been found that these substances also have great experimental utility as constant and abundant emitters of positive ions. The writers have tested various methods of mounting and heating these emitters. They have also analyzed their emission by the use of a mass spectrograph which has been described by Smyth. Separate catalyst samples containing respectively Na, K, Rb, Cs, Mg, Ca, and in one case both Ba and Sr have been shown in this way to emit only the corresponding singly charged positive ion. No doubly charged ions were observed, nor any ions of the other elements composing the catalysts. The alkali metal ions were emitted at lower temperatures than the alkaline earth ions. Particularly in the case of the latter, a preliminary treatment consisting of reduction at red heat in an atmosphere of hydrogen increased the emission.

Emission from hot platinum was also observed consisting of Na^+ and K^+ ions. This was a surface effect and diminished rapidly with time.

Introduction

KUNSMAN[1] has described a new and convenient source of positive ions which is finding many uses in experimental research. This source consists of heated crystal granules of certain catalysts developed for the synthesis of ammonia at the Fixed Nitrogen Research Laboratory in Washington. Briefly, these consist of a fused mixture of iron oxide and about one percent of an oxide of an alkali metal or alkaline earth, with sometimes the addition of about one percent of aluminium oxide. The method of preparation[2] and an x-ray analysis[3] of the crystals have recently been published.

When the crystals are heated they emit positive ions in large numbers. If they are further prepared by reduction in an atmosphere of hydrogen and then glowed and degassed in a good vacuum, the positive ion current is quite constant. This current in a high vacuum is a function of temperature and accurately obeys Richardson's equation, $I=AT^{1/2}\epsilon^{-b/T}$ for thermionic emission. More recently Kunsman has

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[1] Kunsman, Science, **62**, 269 (1925).

[2] Larson and Richardson, J. of Ind. Chem. **17**, 971 (1925).

[3] Wyckoff and Crittenden, J. Am. Chem. Soc. **47**, 2866 (1925).

considerably extended his investigation of the thermionic properties.[4]

For precise experimental work using this type of positive ion source, it is, of course, highly important to have full knowledge of the nature and homogeneity of the ions emitted. The present paper describes a positive ray analysis undertaken primarily to answer this question. Seven samples were investigated, being iron oxide crystals as described, and containing, respectively, caesium, rubidium, potassium, sodium, magnesium, calcium, and, in one sample, both barium and strontium.

APPARATUS

The experimental arrangement[5] is shown schematically in Fig. 1. Some of the sample source under investigation was mounted on a platinum filament at *F*, this being supported by the leads (not shown) which carried the heating current. The arrangement of slits, electric and magnetic fields is obvious. *P* was connected to a Compton electrometer. A mass spectrum was obtained by progressively varying *V* with *H* constant and observing the electrometer current. In most of the experiments the field strength was about 4400 gauss and *V* was varied from 0 to 400 volts. S_2 and S_3 were 6 cm apart. A vacuum of better than 10^{-4} mm of Hg was maintained throughout. The best resolution obtained was not sufficient to separate isotopes, but easily distinguished ions of elements in different rows of the periodic table.[6]

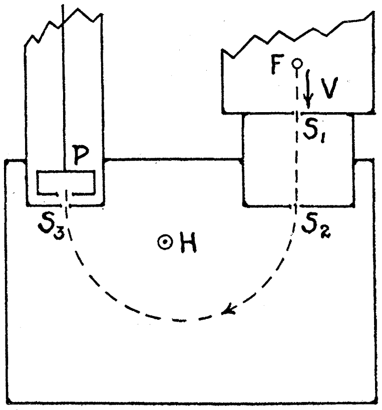

Fig. 1. Apparatus.

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[4] Kunsman, to be published shortly.

[5] The tube used was that described by Smyth, Phys. Rev. **25**, 452 (1925), except that two of the electrodes were removed and the evacuating arrangements simplified.

[6] In two runs the potassium peak indicated by its shape that little more resolving power would have been needed to separate the two isotopes at 39 and 41.

In the course of the experiments four different methods of mounting and heating the catalysts were used. At first the tube was so oriented that the filament and slit S_1 were in the same horizontal plane, a trough with an open side towards S_1 could be used. Later the arrangement was changed so that F was above S_1 as shown in Fig. 1. It was then necessary to turn the trough open side up so as not to spill out the granules and provide small perforations in the bottom for the emission. This method proved less satisfactory, so a narrow, twisted strip of platinum was next mounted and covered as completely as possible with a coating of pulverized catalyst granules. The coating was put on with the aid of paraffin as a vehicle in the same manner as is frequently used in the preparation of oxide coated filaments, the paraffin being vaporized by heating, once the active material is in place. This method has the valuable advantage of providing a large emitting surface.

Although the last mentioned method proved very satisfactory for the alkali metal catalysts, a fourth type of filament was used for those containing alkaline earths. Difficulty was found in coating strip filaments with these. They did not seem to adhere as well as the alkali metal samples. This resulted in an uneven coating so that the heating along the filament was not uniform. Owing to the greater temperatures which had to be used to obtain emission in these cases, this difficulty shortened the life of the filaments considerably. The type of filament finally adopted consisted of a thin-walled platinum tube with small perforations in the side toward S_1 to allow ion emission. This was filled with a finely granulated sample of catalyst and the ends squeezed together to keep it in. The alkaline earth and rubidium samples were investigated in this way.

All of the filaments were less than 1 cm in length. They required heating currents ranging from 4 or 5 amps. for the twisted strip type to 15 amps. for the tube type.

ALKALI METALS

Mass spectra of the emission from the four alkali metal samples are given in Fig. 2. The ordinates, representing electrometer current, are arbitrary and not comparable from one curve to another. This arises from the fact that the electrometer current depended upon the pressure of gas in the path of the ions (which caused scattering), the effective area of the granules mounted on the filament, and the exact position of the latter. It was not possible to have these always the same.

Furthermore no means were available for measuring the temperature of the filament.

Caesium (*132.8*). The mass spectrum of the caesium sample shows a large diffuse peak corresponding to Cs^+ ions. The resolution of the apparatus is not as good for heavy ions as for light, which chiefly accounts for the width of this peak. It is also characteristic of the apparatus that the peak shades off toward lower m/e values. It is quite possible, however, that the shoulder just above 80 is due to Rb^+ impurity. The curve was extended below 50 and very large K^+ and Na^+ peaks observed. These have not been indicated in the figure because it was later definitely established that they came from the platinum filament itself or from a contamination on it from previous samples. Later a new filament was prepared and tested for K^+ and Na^+ before being coated. After this had been coated with some of the caesium sample, a large Cs^+ peak was obtained with little or no K^+ or Na^+.

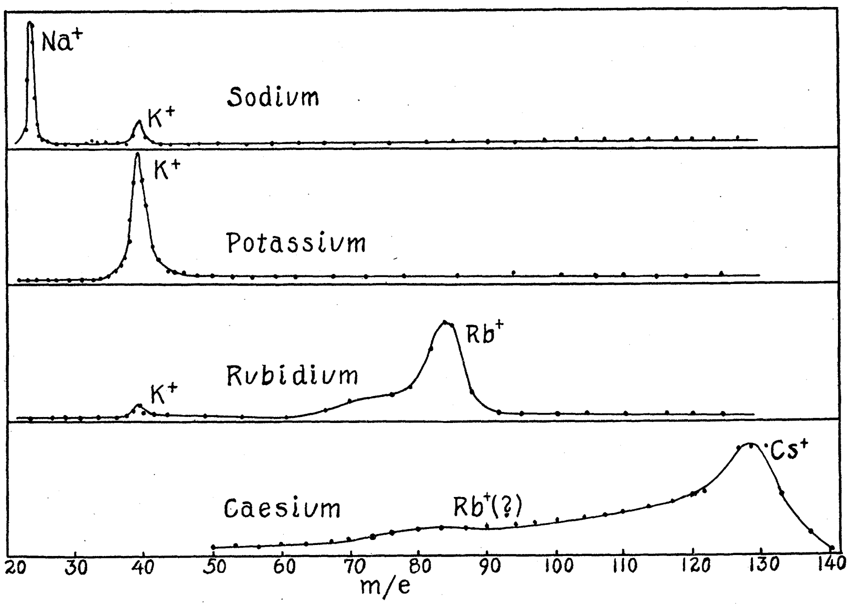

Fig. 2. Mass spectra of catalysts containing alkali metals.

Rubidium (*85.5*). The emission from this sample was at first small. After reduction by the same method as will be described in connection with the alkaline earth samples it was much better. The curve in Fig. 2 shows a run then taken, the only impurity being a small amount of K^+.

Potassium (*39.1*). The curve shows remarkable freedom from the other alkali metals as impurities.[7]

Sodium (*23.0*). The curve of this sample shows a very sharp principal peak indicative of the resolution obtainable at the lower end of the m/e scale. The K impurity was much more pronounced when the filament was first heated, then diminished rapidly and was still diminishing when the curve was taken. It was probably due chiefly to emission from the platinum, of which more will be said below. In the portion of the m/e scale through which a broken line has been drawn, rates of electrometer deflection were not timed. They were observed carefully, however, and it may be said definitely that no peaks comparable with the K^+ peak were to be found.

ALKALINE EARTHS

Mass spectra obtained from the catalysts containing the alkaline earths are shown in Fig. 3. As mentioned above, it was found necessary to go to higher temperatures to obtain characteristic positive ion emission from these substances. Also the emission was greatly increased if they were submitted to a preliminary period of reduction. This was done by mounting the filament in an atmosphere of hydrogen at about 1 cm pressure and heating at a redness just above visibility for about 24 hours. It is possible that the continued heating altered the condition of the sample as well as reducing the surface. Samples so prepared were found to emit singly charged positive ions of the alkaline earths, but in almost all of the runs, certain impurities of sodium and potassium were found which never completely disappeared with time.

In Fig. 3 two characteristic curves are plotted for each sample. The curve marked I represents one of the first runs, which was taken at a low temperature. The procedure then was to increase the temperature and, after a certain lapse of time, to allow conditions to reach a possible state of equilibrium, another run was taken. This process was continued until the filament burned out or the leads became dangerously hot. The curve marked II is a representative run taken at the highest temperature obtainable. The comparative temperatures were judged entirely by the current passing through the filament. The time elaspsing between runs I and II varied with the samples but was of the order of several hours. The impurities were found to decay very rapidly with time, probably exponentially. The ordinates of the curves

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[7] This curve was taken some months before the rest of the work was done. It was mentioned by Kunsman. (Ref. 1.)

of the different substances are again not comparable because the conditions, particularly the temperatures, were not identical.

Barium (137.37) and Strontium (87.63). Curve I shows no evidence of anything but Na$^+$ and K$^+$ which were evidently present as impurities, probably, to a very large extent, coming only from the platinum. Curve II shows a very small peak at K$^+$, a distinct but very broad peak at Sr$^+$, and a very large peak at Ba$^+$. The Sr$^+$ peak is surprisingly small relative to the Ba$^+$ peak, the reason for this being uncertain. No evidence of Sr^{++} or Ba^{++} was found.

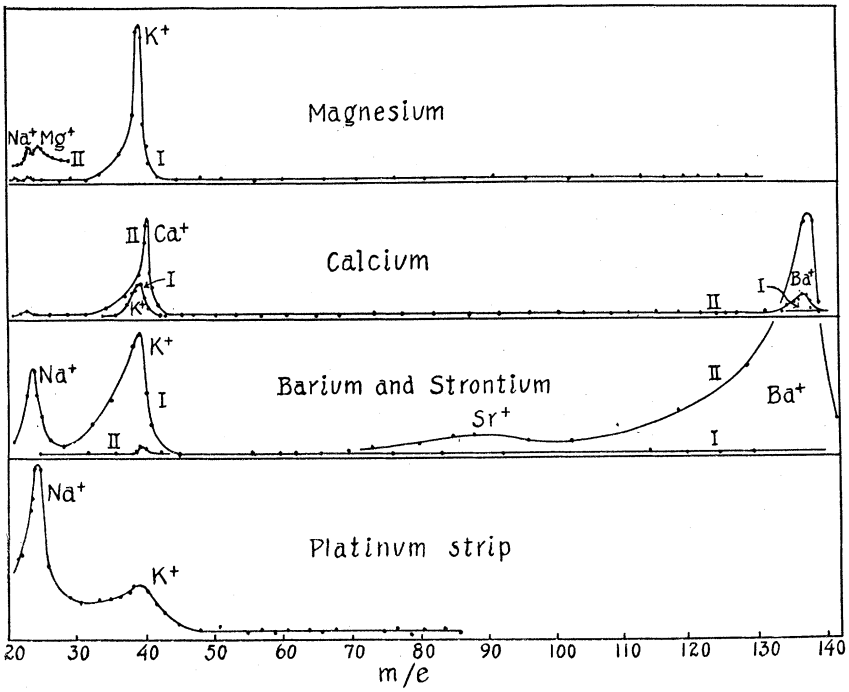

Fig. 3. Mass spectra of catalysts containing alkaline earths and of bare platinum.

Calcium (40.07). Curve I shows only a K$^+$ peak. Curve II shows a very slight Na$^+$ peak, a large peak for Ca$^+$ and a peak of about one-third the height of Ca$^+$, for Ba$^+$. An incomplete run at a slightly higher temperature was obtained in which the Ba$^+$ peak rose relatively to the Ca$^+$ peak. Again no evidence of Ca^{++} or Ba^{++} was obtained.

The rather small shift of the principal peak toward higher m/e in passing from low to high temperatures is perhaps not sufficient in itself to justify the statement that the K$^+$ emission is replaced by Ca$^+$. There is good reason to believe, however, that this shift is genuine.

Furthermore, other evidence is quite in favor of the existence of Ca^+ emission. For example, this 'shifted' peak remained approximately constant at any given temperature, whereas in all cases where K^+ was present as an impurity, the peak corresponding to it diminished rapidly with time. These facts together with the undoubted emission of the other alkaline earths are considered conclusive evidence for the existence of Ca^+ emission.

Magnesium (*24.32*). Curve I shows a small Na^+ peak and a very large K^+ peak. In the following runs the K^+ fell in comparison with the Na^+ peak and they both dropped off with time at constant temperature. In the run at the highest temperature obtained the Na^+ and Mg^+ peaks were distinctly resolved. The filament burned out before the region containing the K^+ peak could be examined. In subsequent runs the filament never lasted long enough at a temperature sufficient to produce Mg^+ to examine in detail the other regions, but no evidence of anything but a K^+ peak was discovered. Voltages high enough to cover the region where Mg^{++} would lie were not used.

Ions From Platinum

The first few runs with the potassium sample of catalyst showed sodium ions also present. Subsequent runs using the same filament charged with caesium catalyst showed sodium and potassium in addition to caesium ions. The filament was taken out and chemically cleaned. It was then replaced and found to emit sodium and potassium ions as before but the caesium had been quite removed. The filament was taken out a second time and heated white hot in a blast flame to volatilize any traces of alkali metals left on the surface by the catalyst samples. In spite of this the sodium and potassium ions still persisted. A new platinum strip was then mounted and this too was found to emit sodium and potassium ions. The first curve obtained in this case is given in Fig. 3.

No particular study was made of this emission of ions by the platinum itself. It was observed however that an increase in the temperature of the strip always produced increased ion emission, particularly of potassium, and that this very quickly diminished if the temperature were then kept constant. It was partly due to the latter fact and partly to care in covering up as much of the platinum surface as possible with catalyst that the sodium, potassium, and rubidium curves show little evidence of this emission.

More extended investigations of the emission from hot platinum have been made by others. A summary of these investigations, together with certain conclusions drawn from the results, has been given by Richardson.[8] The above observations, as far as they go, confirm these conclusions. This is particularly the case as regards the constitution of the ions emitted by platinum, for the present resolving power appears to be better than that of any apparatus heretofore used to study the phenomenon.

DISCUSSION

The mass spectra given in Figs. 2 and 3, together with the circumstances of their production, lead to the conclusion that the only ions emitted in each case were those of the alkali metal or alkaline earth present in the catalyst. The much more abundant iron and oxygen atoms did not appear as ions, nor did aluminium in the catalysts where it too was present. It is interesting that the alkaline earth ions, like those of the alkali metals, were only singly charged, in spite of their possession of two loosely bound valence electrons.

The evidence does not give sufficient basis for much discussion of the mechanism of emission. Very roughly it appeared in the case of the alkaline earths that the lighter elements required higher temperatures to produce emission. Certainly these elements required considerably higher temperatures than the alkali metals. The difficulty seems to vary in the same direction as the ionizing potentials. This may account for the difference in the heights of the barium and strontium peaks.

The chief distinction between these emitters and others is, of course, their constancy and relative inexhaustibility. There is evidently something about their structure which permits the ion-forming atoms to diffuse readily and abundantly to the surface. In most other cases the ion emission rapidly falls off as the supply or at near the surface becomes exhausted.[8]

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[8] Richardson, The Emission of Electricity from Hot Bodies, Chaps. VI and VII.