THE FURNACE SPECTRUM OF BERYLLIUM

By R. F. Paton and G. M. Rassweiler

Abstract

A *high-temperature vacuum furnace* using tungsten for container, and heating elements as well, has been designed to study the furnace spectra of high melting point substances. The furnace spectrum of beryllium in both absorption and emission has been observed from λ2150A–7000A and over a range of temperature up to 2500°K. The prediction that the beryllium line 2348.62A is the first line of the principal series of singlets for the neutral atom has been successfully confirmed and the diffuse and the sharp series of singlets of this element discovered and tabulated.

Introduction

THE work on the spectrum of beryllium before 1921 is conveniently summarized by Kayser and Konen[1] who list only twelve lines for this element. Since that time, new lines have been reported by Glaser,[2] Millikan and Bowen,[3] and others. In this laboratory, an extensive study has been made of the beryllium spectrum by Paton, Sanders, and Albers. They used the vacuum spark source in the wave-length range below 5300A and the spark and arc in air for the range 5000A to 9000A.

The absorption and emission spectra of the element have never been studied with a furnace, though an absorption spectrum by the underwater-spark method has been photographed by Allin and Ireton.[4] They observed the absorption of five well-known multiplets, all unresolved; of the singlet 2348A, unresolved from the triplet 2350A; and of the line 2175A which they claim was first observed in their laboratory by McDonald, Sutton and McLay, but which was actually discovered by Rowland and Tatnall in 1895.[5] Only one of these lines (2348A) is of unknown series identification. Thus, while these underwater-spark data are of considerable interest they do not aid in further work on series relationships.

The only important works on series in the beryllium spectrum are by Back,[6] and Millikan and Bowen. The former studied the Zeeman effect of several lines and made predictions regarding their series relationships although he was unable to set up such series due to the scarcity of observed beryllium lines. Millikan and Bowen, using Back's data together with their own observations in the extreme ultra-violet, succeeded in establishing a set of triplet series of Be I and a set of doublet series of Be II and in calculating the first few term values in each of these series. The singlet series

[1] Kayser and Konen, Handbuch der Spectroscopie, Vol. VII (1924).
[2] Glaser, Ann. d. Physik, **68,** 73 (1922).
[3] Millikan and Bowen, Phys. Rev., **28,** 256 (1926).
[4] Allin and Ireton, Roy. Soc. Can. Trans., **21,** 127 (1927).
[5] Rowland and Tatnall, Astrophys. J., **1,** 14 (1895).
[6] Back, Ann. d. Physik, **70,** 333 (1923).

of Be I have never been published and in fact only two lines, 2348.62A and 4572.69A, have ever been assigned to the singlet system (by Back from their normal Zeeman effect).

It was the purpose of this investigation to design and construct a furnace suitable for the study of the spectrum of metallic vapors, to use this in the study of the absorption and emission spectrum of beryllium, and to see if the data obtained would shed any light on the series identifications of the singlet lines of the neutral atom.

Apparatus and Method

In designing a furnace for this investigation, the need for convenient control of furnace temperatures led to the choice of the electric resistance type. In order to be reasonably sure of securing a sufficient quantity of beryllium vapor, the maximum temperature desired in the furnace was about 2500°C. Both tungsten and carbon will stand such temperatures, and carbon furnaces have been successfully used by King and others. However, a preliminary experiment indicated that beryllium would react vigorously with carbon at high temperatures so tungsten was chosen for the electric resistance heating elements, the furnace being placed in a vacuum chamber to protect the tungsten and beryllium from oxidation.

A furnace of this type requires a high current at a low voltage for the resistance is small and the radiation losses large. The heating elements could not be packed in refractory material, and a satisfactory vacuum maintained at high temperatures. A 30 k.v.a., 25 volt, transformer was available and it remained to design a tungsten container which could be heated to the desired temperatures with the current available. Data on resistivity and radiation losses of tungsten have been published[7] for temperatures up to its melting point. Assuming radiation losses would occur from the outside walls and ends of the container, the surroundings remaining at room temperature, and that heat losses by conduction would be negligible, the power loss for any temperature could be computed. Then knowing the resistance of the tungsten at that temperature, it was possible to find the necessary current and potential drop in the heating elements. Later, tests on the furnace showed the actual temperature for any given current to be about 20 percent lower than the calculated value.

The only part of the furnace which is heated is the tungsten box. This is made up of four strips, 1.6 cm$\times$20 cm$\times$0.07 cm (kindly donated by the Fansteel Products Corporation), each strip forming one side of the box. The ends of the box are open. In order to hold the strips and make electrical contact with them, the ends of each strip are bent outwards at right angles. This makes the box, or tube, formed by the strips 14 cm long and 1.8 cm square in cross section. It is supported in a horizontal position and the beryllium to be vaporized is placed on the bottom strip in a small tungsten boat.

[7] Forsythe and Worthing, Astrophys. J., **61**, 147 (1925).

Fig. 1 shows the arrangement for supporting the tungsten although the strips themselves are not in place. These pass through the small square opening, and are held in place by brass plates screwed to the water-cooled brass blocks. The strips are electrically in series, the blocks being insulated from each other with glass and mica. Surrounding the main portion of the tungsten box is a water-cooled cylindrical radiation shield. The hot tungsten is thus almost completely surrounded by water-cooled brass parts protecting the rubber tubes from direct radiation. The block supports and radiation shield are all mounted on a half-inch brass plate which has a water-cooling chamber on its lower side. A heavy brass box which fits down over the apparatus shown on Fig. 1, constitutes the vacuum chamber. On each side of the box is an observation window of quartz mounted at the end of a brass tube which opens into the furnace directly in front of the end of the tungsten box.

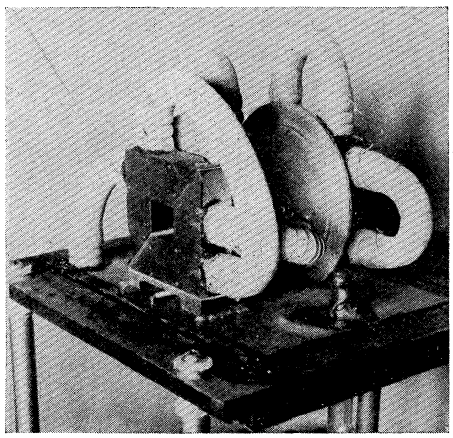

Fig. 1. Photograph of the tungsten furnace.

The temperature of the furnace is controlled by resistance units placed in the primary circuit of the transformer supplying the heating current. Temperatures are measured with an optical pyrometer of the disappearing filament type, the instrument being focussed on the end of the tungsten boat containing the beryllium inside the hot tungsten chamber. Temperature measurements are given to the nearest 50°C.

The operating characteristics of this furnace are very satisfactory. Pressures as low as 5×10^{-5} mm are obtained in the cold furnace and 2×10^{-4} mm at 1000°C. The maximum temperature actually used was 2250°C. High temperatures were never maintained for any longer time than was necessary to secure spectrograms (less than one minute), the brass vacuum chamber heating up rapidly in spite of the water-cooling system. The furnace currents were varied from about 140 amps. at 750°C to 550 amps. at 2250°C.

The continuous source used for the study of absorption effects was the under-water spark between copper electrodes. This was operated with

current from a 4 k.v.a., 60,000 volt, transformer and was intense enough to give exposures in from 8 to 16 seconds over the wave-length range studied (2150A to 7000A).

The spectrograph was a Hilger E1 with quartz optical system. The spectrograms were measured on a Gaertner comparator. In most cases, the measurements were only accurate enough to make identifications positive, but on some plates precision measurements were undertaken using the iron arc for comparison.

Results

Absorption. Observations were made in the wave-length range from 2150A to 7000A in an effort to locate absorption lines of beryllium. The vapor temperature was varied from 1200°C to 2200°C, and over most of this range, exposures were made at intervals of 100°C or less. The only beryllium absorption line which was observed was at 2348.62A. This absorption was first noted on an exposure made through the vapor at a temperature of 1550°C. The next exposure on this plate was at 1850°C and here the line showed as an emission line superimposed on the spectrum from the continuous source. A number of exposures were then made to determine the temperature at which the line would change from absorption to emission. It was found that absorption occurred between the temperatures 1400°C and 1800°C, but was never observed above 1800°C. Emission was observed as low as 1850°C although some exposures at this temperature showed neither absorption nor emission.

It seems remarkable that no other absorption lines should appear in the wide wave-length range studied. It is unlikely that this was due to the lack of sufficient vapor to give the effect, for the quantity of vapor necessary to produce absorption is very small indeed. This is shown by the absorption of a large number of iron lines on two of the spectrograms. The presence of iron vapor in the furnace at that time can only be explained by the fact that the tungsten boat had been ground on an emery-wheel immediately prior to heating the furnace for these pictures. The iron contamination from the emery-wheel must have been minute and the amount of iron vapor from this source very small compared to the beryllium vapor present. Also, the surprising ease with which absorption of 2348A was obtained at low temperatures indicates that only a small quantity of vapor is required to produce absorption. In fact, the absorption of 2348A still occurred after the furnace had been heated six times to temperatures above 1500°C without renewing the supply of beryllium. Whenever the supply of beryllium in the furnace was renewed, a large amount of vapor must have been produced on heating, as evidenced by the fogging of the observation windows.

The absorption at 2348A, and at this wave-length only, makes the series identification of this line quite positive. Its singlet character has already been proven by its normal Zeeman effect; its identity as a member of the principal series is shown by the ease with which it is absorbed, and its position as the first member of this series is demonstrated by the fact that

no other absorption occurred in the wave-length region studied. Thus the prediction of Back and others that 2348.62A is the first line of the principal series of the singlet system of neutral beryllium is confirmed.

Emission. The data on emission are grouped under two heads, namely, lines of previously known series (Table I) and lines whose series identification was made possible by this work (Table II). The former are listed in Table I,

TABLE I. *Emission of lines of known series.*

Wave-length A (air)	Series notation by Millikan	Intensity in furnace 1850°C	2250°C
	Triplet system of Be I.		
3321.35	$2p_1-3s$		
3321.09	$2p_2-3s$	2	8d
3321.02	$2p_3-3s$		
2350.78	$2p-4s$	0	5d
2494.63	$2p_1-3d$		
2494.48	$2p_2-3d$	1	6d
2494.44	$2p_3-3d$		
2175.04	$2p-4d$	—	4d
2650.77 to 2650.47	pp' group	—	2u
	Doublet system of Be II		
3131.07	$2s-2p_2$	—	4
3130.42	$2s-2p_1$	—	5

Note: u = diffuse; d = double but poorly resolved.

where a dash indicates that the line did not appear on any of the plates taken at that temperature. The only triplet lines of neutral beryllium lying in the wave-length region studied are the first two members of the diffuse series and the first two members of the sharp series. These four lines (the term "line" is applied to the multiplet) were observed and also the pp' group at 2650A. There are twelve lines in this region which are known to belong to the doublet system of singly ionized beryllium. Only one of these doublets, the first member of the principal series, was emitted by the vapor in the furnace and this pair faintly and only at the highest temperatures. The three lines in the visible region which appear the most intense in arc and spark sources are 4360.99A (Be II 3^2P-4^2D), 4673.25A (Be II 3^2D-4^2F) and 4572.69A (Be I 2^1P-3^1D). (These were all observed by Albers as intensity 10 in the vacuum spark.) It is interesting to note that neither of the first two lines, which belong to ionized beryllium, was observed on the spectrograms which have been measured. The line 4572A, however, appears with intensity estimated as 12. It is of course not a new observation that the furnace provides a means of sorting out lines emitted by the neutral atom from those emitted by the ionized atom but the fact is nicely illustrated by these data (Table I).

Table II was prepared by carefully analyzing a number of emission plates taken with the furnace at 2250°C in the wave-length region 2150A

to 7000A, computing the wave-lengths from the standard iron lines, then sorting out impurities by the usual methods. Examination of these data together with existing data on beryllium, including that of Sanders and Albers, was then undertaken.

TABLE II. *Singlet lines of Be I emitted at 2500°K*

Int.	λ(air)	ν(vacuum)	First observer	Series
—	8253.5	12112.8	Albers	2^1P-3^1S
12	4572.69	21862.86	Kirchhoff	2^1P-3^1D
5	4408.02	22679.58	Albers	2^1P-4^1S
8	3813.46	26215.49	Sanders	2^1P-4^1D
3	3736.30	26756.86	—	2^1P-5^1S
5	3515.57	28436.78	Sanders	2^1P-5^1D
3	3367.67	29685.62	—	2^1P-6^1D
1	3283.15	30449.80	Sanders	2^1P-7^1D
20	2348.62	42565.15	Rowland	2^1S-2^1P

Term Values

$2^1P-32615.01$	$2^1S-75180.15$	$3^1D-10757.14$	
	$3^1S-20502.21$	$4^1D-\ 6404.51$	
	$4^1S-\ 9940.42$	$5^1D-\ 4183.22$	
	$5^1S-\ 5863.14$	$6^1D-\ 2934.38$	
		$7^1D-\ 2170.20$	

This yielded a list of some fifteen lines that could be tentatively attributed to beryllium. Of these lines five, involving the strongest lines observed, suggested by their order and intensity a series of singlets. A more careful examination gave the typical diffuse series. Of the few remaining strong lines in the region, two, together with a line observed by Albers in the near infra-red, gave the sharp series. The limit of these series was computed by the method suggested by Johanson.[8] The term values are accurate to a few wave-numbers and give an ionization potential for beryllium of 9.277 equivalent volts.

A word should be said about the impurity lines on the emission spectrograms. Nearly all the iron lines which appeared on the two plates previously mentioned had already been assigned by King to Class I in the furnace. A few chromium, mercury, and barium lines also appeared. Two lines at 2397.11A and 2446.47A were attributed to tungsten though the amount of tungsten vapor even at 2200°C must have been minute. It is interesting also that the first five lines of the Balmer series of atomic hydrogen appeared at about 2200°C with estimated intensities of 10, 8, 4, 3, 2, respectively.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS,
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[8] Johanson, Arkiv. f. Mat., Astron. och Fysik., **12**, No. 6 (1917).

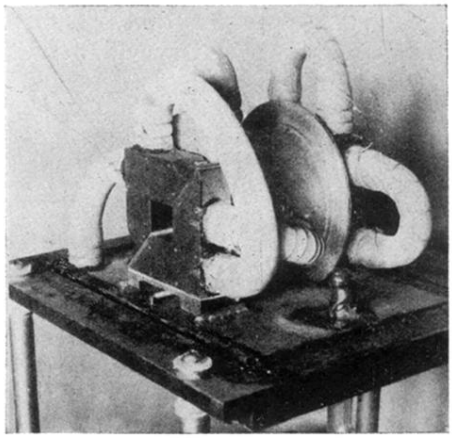

Fig. 1. Photograph of the tungsten furnace.