TABLE II

p-AMINOBENZOATES

R in β-R-ethyl	Yield, %	M. p., °C. base	M. p., °C. picramide	Formula	Nitrogen analyses, % Calcd.	Found	
Methoxy	94	75.9	132.0	$C_{10}H_{13}O_3N$	7.18	7.15	7.24
Ethoxy	93	79.2	136.7	$C_{11}H_{15}O_3N$	6.69	6.40	6.56
Propoxy	87	44.5	138.4	$C_{12}H_{17}O_3N$	6.27	6.20	6.18
Isopropoxy	86	95.4	156.0	$C_{12}H_{17}O_3N$	6.27	6.23	6.30
Butoxy	79	34.0	123.1	$C_{13}H_{19}O_3N$	5.90	6.07	5.71
Isobutoxy	77	..	150.3	$C_{13}H_{19}O_3N^a$	5.90	5.88	5.86
s-Butoxy	84	..	132.5	$C_{13}H_{19}O_3N^b$	5.90	5.87	5.89
t-Butoxy	84	77.4	140.0	$C_{13}H_{19}O_3N^c$	5.90	5.94	5.88

[a] B. p. 176.5–177.5° at 0.7 mm. [b] B. p. 177.0–178.0° at 0.7 mm. [c] B. p. 173.5–174.5° at 0.3 mm.

The picramides were prepared by the method given by Mulliken.[5]

The melting points of the hydrochlorides are not given since they apparently decompose before melting. The bases were all crystallized from ligroin with the exception of the tertiary butoxy compound which was crystallized from a water-alcohol mixture and the isobutoxy and secondary butoxy compounds which solidified after distillation when placed in a cool place for a few days, but these did not give definite melting points and could not be recrystallized. They apparently melt near room temperature. The yields are based upon the amount of glycol ether used.

Physiological data on these compounds will be reported in a later paper.

Summary

Five new β-alkoxy ethyl *p*-nitrobenzoates and a series of eight *p*-aminobenzoates have been prepared and some of their physical constants determined.

MORGANTOWN, WEST VIRGINIA RECEIVED JUNE 29, 1935

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(5) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., 440 Fourth Ave., New York City (1916), Vol. II, p. 32.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Gaseous Discharge Tube Especially Designed as an Intense Source of Continuous Ultraviolet Radiation

BY R. H. MUNCH

In the study of certain gaseous absorption lines, during the course of some research work under the direction of Dr. F. T. Gucker, Jr., the author required an intense source of continuous ultraviolet radiation which was simpler and more efficient than any that could be found described in the literature. This article deals with the development of such a source. Beyond about 3500 Å. there are only three sources of continuous radiation: the so-called Lyman continuum[1] (to 300 Å.), the hydrogen continuum[2] (3657–1216 Å.) and the helium continuum[3] (1125–500 Å.). The hydrogen continuum, which is the most useful, may be excited with considerable intensity if about 1500 v. is applied to an ordinary discharge tube made with a long capillary viewed from the end. Such a tube, dissipating as much as 18 kw., must be made of quartz and water cooled. It is, therefore, expensive and is comparatively inefficient. A more convenient method of exciting the hydrogen continuum without using high voltage and water cooling is by means of thermoelectrons from a hot cathode as in the low voltage arc of Duffendack and Manley.[4] This arc passed between a heated tungsten filament and a disk anode, in a tube containing a palladium tube to admit hydrogen and a quartz window sealed on with wax. We built a tube differing from this only in having an oxide coated

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(1) V. Schumann, "Smithsonian Contributions to Knowledge," **29**, No. 1413, 13 (1903); T. Lyman, *Astrophys. J.*, **60**, 1 (1924); *Nature*, **118**, 156 (1926); G. H. Dieke and J. J. Hopfield, *Z. Physik*, **40**, 299 (1926); *Phys. Rev.*, **30**, 400 (1927); G. Rathenau, *Z. Physik*, **87**, 32 (1933); Collins and Price, *Rev. Sci. Inst.*, **5**, 423 (1934).

(2) V. Schumann, *loc. cit.*, E. Gehrcke and E. Laue, *Ann. Physik*, **76**, 673 (1925); Bay and Steiner, *Z. Physik*, **45**, 337 (1927); Lawrence and Edlefsen, *Rev. Sci. Inst.*, **1**, 45 (1930); Kistiakowsky, *ibid.*, **2**, 549 (1931); Stevens, *ibid.*, **6**, 40 (1935).

(3) J. J. Hopfield, *Astrophys. J.*, **72**, 137 (1930).

(4) Duffendack and Manley, *J. Opt. Soc. Am.*, **24**, 222 (1934); **23**, 101 (1933).

cathode and a thin Pyrex window[5] equivalent to 1 mm. of quartz, but it was too weak a source even with ten times the current Duffendack and Manley used. Starting from this tube we finally evolved a source which combined the intensity of the high voltage tube with the simplicity of the low voltage arc.

Construction and Operation of the Tube.—Figure 1 shows the construction of this tube. The oxide coated cathode, C, is a 0.48 × 15.25 cm. piece of nickel gauze woven of 0.25 mm. wires 19 per inch, bent into a corrugated form having a 0.48 cm. cross section. One end is spot welded to the top of the cathode shield, S, and the other to a 0.10 cm. nickel wire. It is then painted with a water suspension of equal parts of barium and strontium carbonates and dried in an oven. Successive layers are applied until a heavy coating is obtained, since the life of the cathode in a hydrogen tube is proportional to the amount of oxide it has on it.

The cathode is surrounded by a cylindrical shield, S, of 0.125 mm. nickel, 4.06 cm. long and 1.25 cm. in diameter, which forms one lead to the cathode and is closed at the bottom by means of a porcelain disk (cross hatched) through which the second cathode lead passes. The only opening in the shield is a 0.66 × 3 mm. slit cut in a piece of 0.25 mm. sheet tungsten[6] welded in the side.

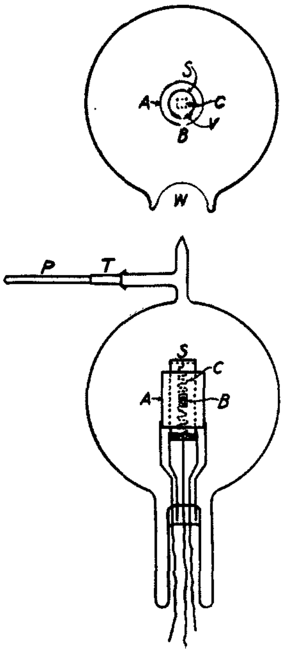

Fig. 1.

The anode, A, is a 2.2 × 2.86 cm. nickel cylinder made from 0.25 mm. sheet with a 0.32 cm. × 0.64 cm. hole, B, to correspond with the slit in the cathode shield. These parts are mounted as shown on a five wire stem which is then sealed into a 10 cm. Pyrex bulb. When the tube is in operation, the whole discharge between the cathode and the anode must pass through the small slit in the shield, and is viewed through the opening in the anode. This arrangement of parts gives a rectangular light source most suitable for a spectrograph or any instrument having a collimating slit. The extremely efficient source of electrons furnished by the oxide coated cathode, together with the short distance between anode and cathode, enable this tube to pass a given current at about 5% of the voltage required for an ordinary capillary tube. It requires no water cooling and could operate continuously at a current of 1.5 amp., or run for a short time at a higher current. Since the slit area was 2 sq. mm., the current density through the slit was 75 amp. per square centimeter for continuous operation and could be increased considerably for short periods. The use of a smaller slit was not practical, since it made the discharge hard to start.

The thin window, W, is made opposite the slits by first blowing a bubble about 3.2 cm. in diameter, then melting it back to about half its height and sucking it in carefully. The palladium tube, P, is now silver soldered to a copper tube, T, the end of which is flared and sealed on the *outside* of a piece of Nonex which is fused to the Pyrex from which the bulb is made. The external copper seal withstands sudden heating without developing cracks. The tube must now be evacuated and freed of all traces of moisture or carbon monoxide which might deactivate the cathode and would certainly produce line or band spectra. It is connected through a liquid air trap and large stopcock to a vacuum pump. The glass and metal parts are outgassed thoroughly by passing a discharge through the tube and sweeping it out with a stream of hydrogen at 2–4 mm. pressure. This is admitted by holding a Bunsen burner flame under the palladium tube, and its removal is regulated by the stopcock. When the spectrum becomes continuous, below 3657 Å., the tube is sealed off.

The electrical connections are similar to those of a "tungar" or a hot cathode mercury arc rectifier. The cathode, which requires 9 amp. at about 3 v., is supplied by a step-down transformer and connected in series with a rheostat and ammeter. The anode circuit, also containing a rheostat and ammeter, may be connected to any 110 volt circuit. The use of a. c. to heat the cathode and d. c. for the anode circuit gives the maximum cathode life. In operation, the fall of potential between anode and cathode is 30–35 v. If the discharge fails to start (before the tube has been outgassed or when the cathode is nearly spent) it may be started by touching the palladium tube with the type of Tesla coil used in testing for leaks in a vacuum system.

Performance of the Tube.—The improved hydrogen arc was found to be about thirty times as intense (for the same current) as the original type of Duffendack and Manley. Since the latter only used 50 m. a. as against 1.5 amp. as a moderate rating for the improved type, the total increase is about nine hundred fold since the intensity is proportional to the current density.[7]

We did not have the equipment necessary to compare the improved lamp with the high voltage arc, but if the intensity here also is proportional to the current, the increased efficiency of the new tube can be judged by the fact that it passes 1.5 amps. for about 75 watts total energy, instead of over 2 kw.

The determination of the absolute intensity of the continuum emitted by the lamp was outside

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(5) Simon Sonkin, *J. Opt. Soc. Am.*, **19**, 65 (1929).

(6) When the slit was made in the nickel, or even in a molybdenum section, its edges melted and lines appeared in the continuum. Tungsten proved completely satisfactory, although harder to work. It must be cut with a thin abrasive wheel, since shears splinter it. The slit was cut by means of carborundum dust on a copper disk run at high speed.

(7) Bay and Steiner, *loc. cit.*; Lawrence and Edlefsen, *loc. cit.*

the scope of our work. However, a comparison was made with the mercury arc lines emitted by a G. E. "Labarc" when both sources were run at 1 amp. The continuum was 25% as intense as the 2483 and 2652 Å. lines, 7% as intense as the 2894 and 3022 Å. lines and 12% as intense as the 3350 Å. line. These figures should give anyone familiar with this field a satisfactory idea of the performance of the lamp.

The Tube as a Line Spectral Source.—This type of lamp operates when filled with helium, argon, or a mixture of argon and mercury; and presumably when filled with the other rare gases. The argon mercury mixture gave a spectrum from which the far ultraviolet lines, particularly the resonance line, were nearly absent due to the quenching effect of argon while the visible and near ultraviolet lines were very strong.

Acknowledgments.—The author wishes to express his appreciation to Dr. F. T. Gucker, Jr., for his encouragement and assistance in the course of this work and for his assistance in the preparation of the manuscript for publication. It is also a pleasure to acknowledge the helpful advice given by Dr. R. A. Fisher and Dr. W. S. Huxford of the Physics Department of Northwestern University.

Summary

A simple, low voltage hydrogen discharge tube especially designed as an intense source of continuous ultraviolet has been developed. It requires no water cooling, since it produces the same light intensity with only about 5% of the electrical power required by a high voltage hydrogen discharge tube. Details of construction and operation are given.

In addition to being useful as a source of continuous radiation it has been used as a source of the line spectra of mercury and the rare gases.

EVANSTON, ILLINOIS RECEIVED JUNE 22, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Some Thermodynamic Properties of Uni-univalent Halide Mixtures in Aqueous Solution

BY HERBERT S. HARNED

It has been shown experimentally by Güntelberg and by Harned that the logarithm of the activity coefficient of hydrochloric acid in chloride mixtures of constant total ionic strength varies linearly with the molality of the acid. Since these earlier studies, other investigations have confirmed this result.[1]

Recently, from a number of sources, sufficient evidence has been acquired to permit more extended observations of this relation, particularly with respect to concentration and temperature. The results obtained will have a special interest in connection with some recent generalizations made by Åkerlöf[2] regarding the behavior of these mixtures. Of still greater interest will be the limitations which the newer knowledge imposes upon Brönsted's theory of the specific interaction of ions.[3]

For our purposes, the law of the linear variation of the logarithm of the activity coefficient at constant ionic strength may be expressed for the systems of uni-univalent halide acid–halide salt mixtures in the following manner. Thus

$$\begin{aligned} \log \gamma_1 &= \alpha_1 m_1 + \log \gamma_1{}^0 = \log \gamma_{1(0)} - \alpha_1 m_1 \\ \log \gamma_2 &= \alpha_2 m_2 + \log \gamma_2{}^0 = \log \gamma_{2(0)} - \alpha_2 m_2 \end{aligned} \qquad (1)$$

where the ionic strength, $\mu = m_1 + m_2 =$ constant. The first of these equations refers to the acid (subscript 1) in the mixture, and second to the salt (subscript 2) in the same mixture. $\gamma_1{}^0$ and $\gamma_2{}^0$ are the activity coefficients of the acid at zero concentration in the salt solution and that of the salt at zero concentration in the acid solution, respectively. $\gamma_{1(0)}$ and $\gamma_{2(0)}$ are the activity coefficients of the acid and salt in pure aqueous solution of the acid and salt, respectively. Equation (1) is taken to be valid at any total ionic strength, μ.

The present communication contains measurements of the cells

H_2 (1 atm.) | HCl (0.01), NaCl(m) | AgCl | Ag Type I

which will serve to supplement the available accurate data on this subject. Results have been

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(1) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned, THIS JOURNAL, **48**, 326 (1926); see also Harned and Mason, *ibid.*, **53**, 3377 (1931); Hawkins, *ibid.*, **54**, 4480 (1932); Mason and Kellam, *J. Phys. Chem.*, **38**, 689 (1934); Bates and Urmston, THIS JOURNAL, **55**, 4068 (1933); Murdoch and Barton, *ibid.*, **55**, 4074 (1933).

(2) Åkerlöf and Thomas, *ibid.*, **56**, 593 (1934); Åkerlöf, *ibid.*, **56**, 1439 (1934).

(3) Brönsted, *ibid.*, **44**, 877 (1922).