(probably diacetyl peroxide) suggests that the main chain-terminating reaction is the combination of two acetate radicals.

It is of course possible that the attack of the hydroxyl radical on acetone may be represented by the equation

$$OH + CH_3COCH_3 \longrightarrow CH_3COOH + CH_3 \quad (11)$$

instead of (4), followed by equations (2) and (3). This would also represent correctly the chemical course of the decomposition, especially if we assume that reactions (4) to (8) occur to a small extent as side reactions producing diacetyl peroxide; however, we believe that equation (4) is to be preferred to equation (11).

Summary

1. The products of the photochemical oxidation of gaseous acetone at 100° with the full radiation from a mercury vapor lamp are acetic acid and formaldehyde; the formaldehyde is largely oxidized to carbon dioxide and water; there are smaller amounts of organic peroxides formed.

2. The quantum yield of the oxidation process has been found to be about 0.3, approximately ten times the quantum yield of the photochemical decomposition in presence of carbon dioxide in the same system.

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RECEIVED JULY 22, 1938

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

The Oxide-coated Filament. The Relation between Thermionic Emission and the Content of Free Alkaline-earth Metal

BY C. H. PRESCOTT, JR., AND JAMES MORRISON

Introduction

The oxide-coated filament had its beginning in the sealing-wax era of vacuum technique. The obscure accident of its origin is not recorded, but all of our older physicists knew that an enhanced emission of electrons could be obtained by smearing sealing-wax on a platinum ribbon and burning it off in air. The first authentic study is recorded by Wehnelt,[1] who investigated the voltage-drop in a gas discharge tube with cathodes coated with various metallic oxides. Its further evolution and development to the status of a cathode in Western Electric vacuum tubes has been described by H. D. Arnold.[2] A comprehensive treatment of its history, the various modifications in current use, and divergent theories of its preparation and behavior has been given by Saul Dushman[3] in a treatise on "Thermionic Emission." A later review is given by J. H. deBoer.[4]

The present work is devoted to a quantitative determination of the relation between thermionic emission and the content of free alkaline earth metal. To this end we have employed a filament which is a platinum rhodium core coated with barium, strontium, and nickel carbonates. On heating in a reducing atmosphere this coating becomes a grossly homogeneous colloidal mixture of barium oxide, strontium oxide, and free nickel. After a thorough preliminary clean-up of the experimental tube, the requisite amounts of free alkaline-earth metal are generated by reaction with methane. The electrical measurements are summarized by the use of the Richardson equation for thermionic emission. Free alkaline earth metal has been determined by oxidation with carbon dioxide and analysis of the gaseous reaction products.

Acknowledgment is due to Mr. V. L. Ronci and his staff for their care in the assembly of the vacuum tubes used in these studies.

Experimental Procedure

The experimental tube used for these studies, as shown in Fig. 1, contains a filament whose core is a 0.0127-cm. wire of 80% platinum and 20% rhodium. The coating was applied by passing the core through a suspension of barium carbonate, barium nitrate, strontium carbonate, and basic nickelous carbonate in amyl acetate and pyroxylin. Three coats were applied after each of which the filament passed through an oven at 675° in an atmosphere of carbon dioxide. The coating vehicle largely evaporated and the fusion of barium nitrate gave the coating enough adherence to undergo the processes of assembly. The final coating is 0.0025 cm. thick to as close as we can determine.

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[1] A. Wehnelt, *Ann. Physik*, **14**, 424 (1904).

[2] H. D. Arnold, *Phys. Rev.*, **16**, 70 (1920).

[3] Saul Dushman, *Rev. Modern Phys.*, **2**, 381 (1930).

[4] J. H. deBoer, "Electron Emission and Adsorption Phenomena," Cambridge University Press, Cambridge, England, 1935.

The filament is mounted in the common axis of three cylindrical nickel plates. The central cylinder is the anode used in the measurements; the other two serve as guard rings to define a radial field about the segment of filament whose emission is measured. The filament core is scraped bare for 0.475 cm. from the welds, which just suffices to concentrate the end cooling in the bare segments. As a result the coated area runs at a uniform temperature, which is essential to ensure uniform activation and so give significance to the determination of free alkaline earth metal. Small holes (as shown in Fig. 1) are bored in the plates to permit temperature measurements of the filament which is held taut by a large molybdenum spring.

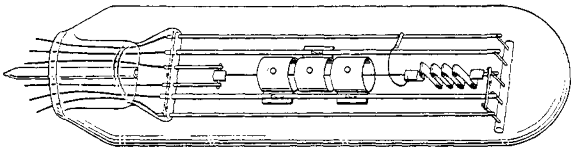

Fig. 1.—The experimental tube.

The physical dimensions of the filament and experimental tube are given in Table I.

Table I

Coated length	4.125 cm.
Plate length	0.9524 cm.
Filament core radius	.00635 cm.
Coating radius	.00889 cm.
Plate radius	.475 cm.
Coating area	.2305 sq. cm.
Emitting area	.0532 sq. cm.
Volume of bulb	245 cc.

With the exception of the filament, all metal parts, prior to assembly, were baked for four hours at 1200° in a stream of hydrogen, saturated with water at room temperature. This procedure was designed to burn out such impurities as carbon and sulfur. This treatment was found necessary in order to avoid spurious activation and large blanks in the determination of free alkaline earth metal.

We still encountered spurious activation by reaction of the oxides with carbonaceous residues from the coating bath. This necessitated a rigorous conditioning treatment. After the tube was baked out, and the plates outgassed by heating with induced high frequency current, the filament was glowed in successive samples of carbon dioxide. This treatment was continued until the carbon monoxide formed was reduced to about 0.05 cc. mm. (cubic centimeters at one millimeter pressure). The preliminary conditioning treatment is given in detail in Table II. Treatments are *in vacuo* except as specified.

Table II

1. Baked 60 min. at 400–425°
2. Glowed filament, 5 min. at 1000°
3. Glowed filament, 30 min. at 900° in 5 cc. mm. CO, 10 cc. mm. CO_2
4. Heated plates, 5 min. at 850°
5. Heated plates in 0.5 mm. H_2, 5 min. at 850°
6. Heated plates, 5 min. at 850°
7. Glowed filament in 10 cc. mm. CO_2, 30 min. at 900°
8. Baked 45 min. at 400°, measured rate of gas evolution to ensure substantial clean-up
9. Heated plates, 850°, measured rate of gas evolution
10. Glowed filament in 1–2 cc. mm. of CO_2, 30 min. at 900° and analyzed the gaseous products

The filament was activated by glowing for fifteen minutes at an uncorrected temperature of 900°, in a sample of methane. The methane was substantially decomposed, giving hydrogen and carbon monoxide, which indicate the chemical reaction

$$CH_4 + BaO = Ba + CO + 2H_2 \text{ or}$$
$$CH_4 + SrO = Sr + CO + 2H_2$$

Some of the active metal formed evaporated from the filament and reëvaporated from the plates, either during formation or in the subsequent stabilization treatment. Due to the "gettering" action of this evaporated metal, carrying down some of the gases, the reaction products were not quantitatively recovered for analysis.

Before taking electrical measurements it was necessary to denude the tube of gas and to permit diffusion to bring the filament coating into an equilibrium state. A liquid air trap was used to keep mercury vapor out of the tube during the measurements. This conditioning and stabilizing treatment is given in detail in Table III.

Table III

1. Heated plates, 3 min. at 800°
2. Baked 15 min. at 350°
3. Removed mercury vapor by use of liquid air, contd. bake for 15 min., fil. at 700° during last 5 min. of bake
4. Heated plates, 3 min. at 800°
5. Glowed filament, 15 min. at 900°
6. Glowed filament, 60 min. at 800°, 80 v. potential on plate

After the emission current at 800° and 80 v. had remained stable for a period of at least thirty minutes, the currents to the central plate were measured at a series of temperatures between 700 and 800°.

When the emission measurements were completed, the liquid air was removed, and the filament subjected to successive treatments in samples of carbon dioxide which were each collected for analysis. The total carbon monoxide found was taken as a measure of the free alkaline earth metal according to the reaction

$$CO_2 + Ba = BaO + CO$$

During this treatment a considerable proportion of the carbon dioxide was converted to barium and strontium carbonates. It should be noted, however, that the amounts were small as compared to the total amounts of barium and strontium oxides. These carbonates were subsequently decomposed and the carbon dioxide recovered, as the filament was glowed for approximately twenty minutes while the gases were pumped off for analysis.

Four tubes used in this study were each activated three times in methane and deactivated by treatments with carbon dioxide.

The Temperature Measurements

Temperatures were measured with an optical pyrometer of the disappearing filament type following in general a design by Forsythe.[5] This was calibrated from 700 to 1200° against a standard lamp obtained from the Bureau of Standards. A screen of Corning Pyrometer Red glass (effective wave length 0.66 μ) was used for temperatures above 800°. Below this temperature no screen was used, but no errors are introduced due to the predominantly red character of the light. The uncertainties in the temperature measurements are about 5°, which is within the limits of other errors in dealing with the oxide-coated filament.

Corrections were applied for a 90% transmission of the glass bulb and the emissive power of the filament which was approximately 64%. Since the sum of the emissive power and reflectivity is unity, we have been able to compute the emissive power from the diffuse reflectivity determined by a method analogous to that employed by Worthing.[6] Details of these measurements are described in another article.[7]

The experimental reflectivity (after the preliminary treatments) is approximately 36% both at room temperature and under operating conditions. There is little if any change due to activation, *i. e.*, formation of free alkaline earth metal. There is a gradual rise with time due to glowing at 900° which may be due to gradual sintering or slight loss of nickel. This introduces an uncertainty no greater than that already indicated in the temperature measurements.

The Measurements of Thermionic Emission

During emission measurements the tube was open to the vacuum pumps but protected from mercury vapor by a liquid air trap. After the filament was outgassed and stabilized, the thermionic emission was measured at a series of potentials from 0 to 100 v., and at several uncorrected temperatures ranging from 700 to 800° (corresponding to 998 to 1103°K. true temperature). Below 700° the filament could not be seen in the optical pyrometer, and above 800° the activity was unstable. At 900°, in particular, the activity rapidly dropped to a lower level, presumably characteristic of a dynamic steady state involving evaporation of active metal from the filament surface, but it recovered in a few minutes of aging at 800°. We thus were limited to a range of 100° in the region of normal operating temperatures. In this range, however, the measurements characteristic of a given state of the filament were entirely reproducible to within the limits of the temperature measurements.

Since the field within the collecting anode is strictly radial, the limiting case of temperature saturation where the current is limited by space-charge should follow the slope of the Langmuir space-charge equation.[8] This is a linear relation between the two-thirds power of the current and the applied voltage. Figures 2 and 3 show typical examples of the current-voltage relations, the two-thirds power of the current being plotted against the applied voltage. The theoretical slope is indicated by the broken line.

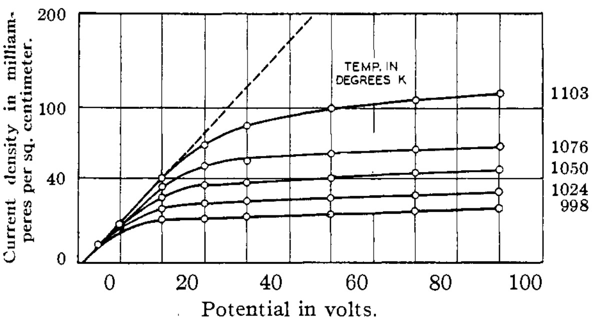

Fig. 2.—Tube A, state 4: two-thirds power of current density *vs.* applied potential.

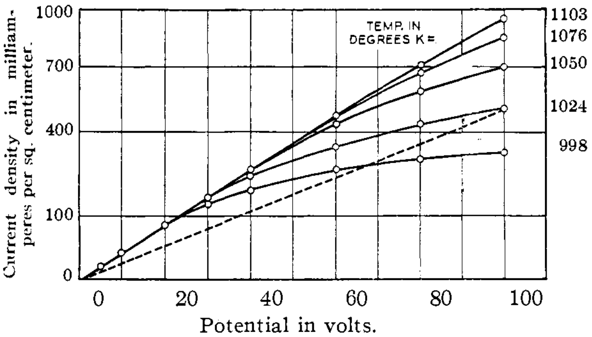

Fig. 3.—Tube C, state 3: two-thirds power of current density *vs.* applied potential.

We may note (as in Fig. 3) that, as the filaments become more active, the currents rise above the limiting values indicated by the Langmuir space-charge equation. Such an effect suggests such factors as gas ionization and spurious paths by which electrons could reach the anode. But these do not seem probable and should give curved relations and not the limiting straight lines found in all cases by experiment. We may note, however, that the theory is idealized in that it neglects the initial velocities of the electrons due to thermal agitation, and that the actual filament is rough in texture and may not conform to the theoretical conditions. It will require further work to elucidate this effect.

At higher potentials the space-charge is swept out and this region of the curves corresponds to

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(5) W. E. Forsythe, *Astrophys. J.*, **43**, 295 (1916).

(6) A. G. Worthing, *Phys. Rev.*, **10**, 377 (1917); *Z. Physik*, **22**, 9 (1924).

(7) To appear in the *Journal of the Optical Society of America.*

(8) I. Langmuir, *Phys. Rev.*, **2**, 450 (1913); Langmuir and Blodgett, *ibid.*, **22**, 347 (1923).

voltage saturation where the current is limited by the activity of the filament. In this case the emission conforms to the Richardson equation.[3]

$$i = AT^2e^{-\epsilon\phi/kT}$$

where A and $\epsilon\phi/k$ are empirical constants and ϕ (the thermionic work function) may be interpreted as the work required to remove an electron from the filament. Plotting $\log i - 2 \log T$, for the currents at 80 v., against the reciprocal temperature, as in Fig. 4, gives a family of straight lines, one corresponding to each activation state of the filaments studied. Four curves have been omitted which practically coincide with those shown in the high activity region. The deviations at higher temperatures for the more active states show the influence of space charge. With this exception the data may be summarized completely by two families of parallel straight lines, one for the active states and another for the inactive states following the preliminary clean-up. The two corresponding values of the work function are 1.37 and 1.64 v., respectively. The values of A would be given by the intercepts on the axis where $T = \infty$. These intercepts are, however, so far (on the graphs) from the region of observation that the different heights of the lines may be due in part to small changes in work function, and the absolute values of A as obtained by extrapolation would be doubtful. We have therefore taken as our measure of activity the currents corresponding to the ordinates of the lines at 1050°K. These are plotted in Fig. 6 against the content of free alkaline earth metal determined by analysis.

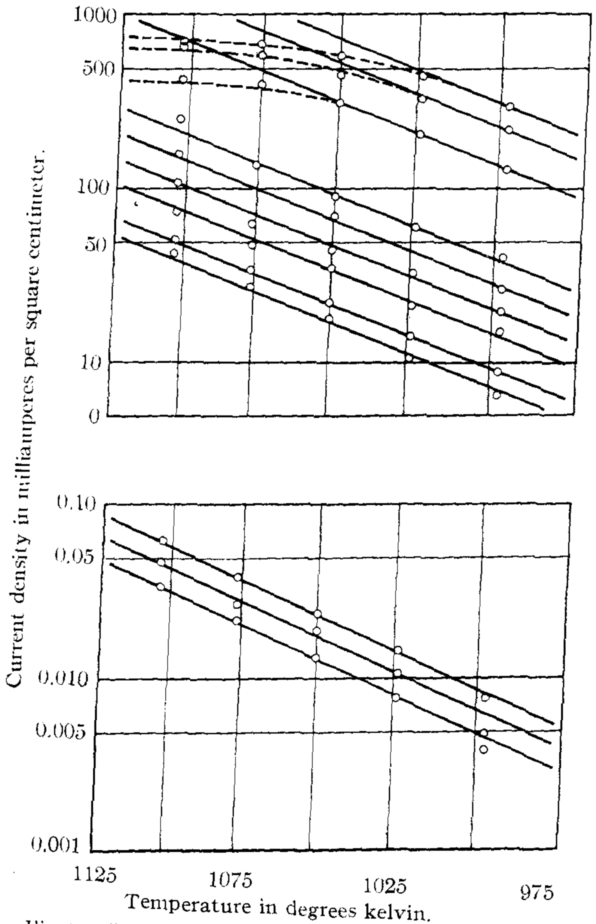

Fig. 4.—Current temperature relation for various active states. Log i/T^2 *vs.* $1/T$ according to the Richardson equation.

The Gas Analyses

The nucleus of the experimental methods is the equipment for gas analysis, a refinement of apparatus described by one of the authors.[9] The essential features are shown in Fig. 5. The gas for analysis is collected by a Toepler pump and measured in a capillary pipet, Fig. 5a, which operates in a fashion similar to a McLeod gage. The gas is then allowed to escape and is circulated through the absorption train. The gas is circulated by operation of the same Toepler pump and again collected for measurement. The reagents used in these analyses are copper oxide at 300°, magnesium perchlorate and soda

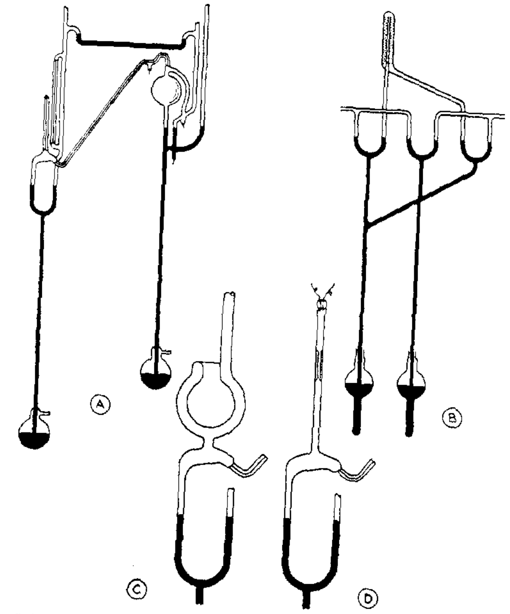

Fig. 5.—Details of the gas analysis apparatus.

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[9] C. H. Prescott, Jr., THIS JOURNAL, **50**, 3237 (1928).

lime. These may be switched in and out by mercury cut-offs as shown in Fig. 5b. Auxiliary equipment includes a platinum ribbon filament in a water-cooled tube, and the explosion pipet shown in Fig. 5d with which is associated another Toepler pump. Mixtures containing H_2O, CO_2, H_2, CO, and O_2 or CH_4 can be analyzed completely. The oxygen analysis by means of the platinum filament requires an excess of hydrogen or carbon monoxide. Methane cannot be exposed to the hot filament and consequently cannot be determined when oxygen is present. When oxygen is absent, methane, which is not affected by any of the reagents, is finally mixed with oxygen and exploded. With the tubes of reagents well outgassed the sensitivity of the apparatus is about 0.02 cc. mm. (cubic centimeters at a pressure of one millimeter of mercury). This is equivalent to 0.03 microgram of carbon monoxide, approximately the amount in one square centimeter of a monomolecular layer. The accuracy, which we definitely sacrificed to sensitivity, is about 2% except on the smallest samples.

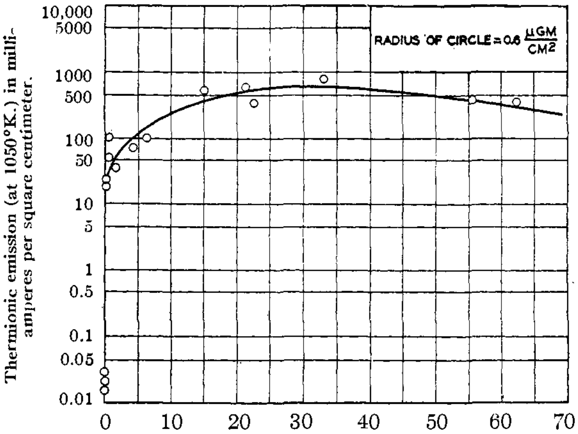
The experimental tube and the liquid air trap are mounted as shown in Fig. 5c on a structure similar to the two pipets. Methane or carbon dioxide is pumped in by a third Toepler pump. During reaction the gas is entirely confined within the experimental tube, since the mercury is raised up into the stem of the tube completely filling the space of the liquid air trap. During thermionic measurements the mercury level is drawn down to permit liquid air to be placed in the trap and connection made to the high vacuum line.

The determination of free alkaline earth metal requires, in general, four or five successive treatments of thirty minutes in carbon dioxide at 900°, following each of which the gas is recovered for analysis. For the smaller amounts of active metal this has sufficed to reduce the carbon monoxide found to about 0.02 cc. mm., which appears to be a mean blank determination for the tube and analytical apparatus, and is close to the ultimate sensitivity of the method.

This blank raises a question as to a possible reaction between carbon dioxide and nickel

$$\mathrm{Ni} + \mathrm{CO_2} = \mathrm{NiO} + \mathrm{CO} \qquad K = p_{\mathrm{CO}}/p_{\mathrm{CO_2}}$$

The equilibrium constant may be computed from data on the reduction of nickel oxide by hydrogen[10] and the water gas reaction.[11] At 1209°K., the true temperature of the carbon dioxide treatments, this is 0.012. The lowest value of the CO–CO_2 ratio in our analyses is 0.017, while several of the low terminal ratios were twice the equilibrium value. Noting that the equilibrium is independent of total pressure, this indicates that no nickel could have reacted. We thus judge this residual carbon monoxide to be a spurious evolution, possibly not even coming from the filament.



Amount of active metal in micrograms per square centimeter of equivalent barium.

Fig. 6.—Thermionic emission *vs.* content of free alkaline earth metal.

In Table IV, following a summary of the corresponding thermionic data, we have shown the complete analytical results. Each tube is designated by a letter and each successive state of activity by a subscript. In estimating the total free alkaline earth metal for each state of activation, we have considered the results of those analyses prior to a value equal to or less than 0.02 cc. mm. subtracting 0.02 cc. mm. from each determination before summing. These are equivalent to the amounts of free alkaline earth metal shown as equivalent weights of barium.

In the fourth tube, used only for states with large amounts of active metal, the preliminary clean-up was abbreviated and the corresponding initial activity was ignored because of the uncertainty of its state. It was found that after active metal was once permitted to escape within the tube we could not reëstablish the low level of initial activity without cleaning up the whole tube again. Metal deposited on the plates redeposited on the filament when the plates were out-gassed prior to the activity measurements. Thus we have two active states B_3 and B_4 which

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(10) Pease and Cook, THIS JOURNAL, **48**, 1199 (1926).

(11) Emmett and Schultz, *ibid.*, **52**, 1782 (1930).

TABLE IV

SUMMARY OF ANALYTICAL DATA

	A_1	A_2	A_3	A_4	B_1	B_2	B_3	B_4	B_5
Current at 1050°K., ma./sq. cm.	0.0127	65.5	33.6	46.7	0.0228	21.4	94.7	16.8	564
ϕ, v.	1.64	1.37	1.37	1.37	1.64	1.37	1.37	1.37	1.37
A, amp. cm.$^{-2}$ deg.$^{-2}$	0.00082	0.221	0.114	0.157	0.00148	0.0720	0.319	0.0570	1.90
CH_4 consumed, cc. mm.	.....	0.71	0.28	1.73	.....	0.072	...	...	2.60
CO recovered, cc. mm.	.....	0.64	0.35	0.87	.....	0.059	...	...	1.68
Analyses, cc. mm. of CO		.093	.067	.037		.022	.028		0.483
		.059	.018	.014		.018	.028		
		.026	.020			.020	.015		
		.032					.038		
		.021					.015		
Blank, cc. mm. of CO		.020	.020	.020		.020	.020		
Total Ba + Sr, cc. mm. of CO		.13	.05	.02		.00	.02		(0.66)
Equivalent Ba, μ g.		.97	.35	.13		.00	.12		(4.89)
Equivalent Ba, μ g./sq. cm.		4.2	1.5	.5		.0	.5		(21.2)

	C_1	C_2	C_3	C_4	D_2	D_3	D_4
Current at 1050°K., ma./sq. cm.^{2}	0.0173	352	727	527	91.4	314	381
ϕ, v.	1.64	1.37	1.37	1.37	1.37	1.37	1.37
A, amp. cm.$^{-2}$ deg.$^{-2}$	0.00112	1.19	2.45	1.78	0.309	1.06	1.29
CH_4 consumed, cc. mm.	......	3.27	1.32	0.70	.41	2.13	3.94
CO recovered, cc. mm.	......	2.49	0.85	.41	.23	1.68	2.71
Analyses, cc. mm. of CO		1.240	.823	.383	.115	0.487	1.343
		0.258	.140	.077	.072	.131	0.274
		.141	.074	.056	.049	.064	.192
		.117	.054	.039	.038	.067	.121
		.072	.041		.026	.054	.108
Blank, cc. mm. of CO		.020	.020	.020	.020	.020	.020
Total Ba + Sr, cc. mm. of CO		1.73	1.03	.48	.20	.70	1.94
Equivalent Ba, μ g.		12.77	7.62	3.51	1.46	5.20	14.32
Equivalent Ba, μ g./sq. cm.		55.4	33.1	15.2	6.3	22.6	62.2

were obtained by reëvaporation of active metal and without use of methane. We should note, however, that this scattered free metal did not interfere with our analyses; the carbon dioxide would not react even with the active filament except at elevated temperatures. For the state B_4 we have no analysis since there was already indication that the amount of active metal was below the sensitivity of our apparatus. One further point, B_5, we have wished to include as corroborative of the other activities in its neighborhood. The tube was lost after the first analysis for this determination. But the course of successive analyses is so smooth that we have felt justified in estimating the total amount by comparison of the first analyses and interpolation between the total amounts for its neighbors.

Discussion

The results tabulated in Table IV are shown in Fig. 6 which expresses the correlation between thermionic activity (measured by the current density at 1050°K.) and the content of free alkaline earth metal. This latter is expressed as the equivalent micrograms of barium per square centimeter of superficial filament surface. The radius of the circles, 0.6 μ g./sq. cm., is equivalent to 0.02 cc. mm., the sensitivity of the gas analysis methods. The actual errors are somewhat larger, being the accumulations from several analyses each.

The lowest activity values, 20 microamperes per sq. cm., are still doubtless associated with free barium, formed by spurious activation, but an amount much less than our analytical limit of sensitivity. In the neighborhood of this limit, which corresponds to 0.6 μ g./sq. cm., the activity is 30 m. a. per sq. cm. The curve then rises to a value of 600 m. a. per sq. cm. which may be a maximum in the neighborhood of 30 μ g./sq. cm. But this maximum is not definitely established, and the most significant feature of the relation is its flatness from 15 to 60 μ g./sq. cm.

Taking a monomolecular film of barium as 0.14 μ g./sq. cm., the range 0.6-15-60 μ g./sq. cm.

is equivalent to 4-100-400 atomic layers upon the geometrical surface. Minute amounts of metal appear largely to saturate the active surfaces from which electrons are emitted. These may be the surfaces either of nickel or oxide particles. Further addition of active metal contributes little to thermionic activity, but provides a reservoir of active material.

Previous analyses of free alkaline earth metal in vacuum tubes are reported by Berdennikowa,[12] Clausing[4] (p. 348), and Fritz.[13] The water vapor method of Berdennikowa does not discriminate between active metal in the filament and elsewhere in the tube. The same criticism seems to apply to Clausing. Barium nitride formation and microanalysis, as employed by Fritz, appear selective but less sensitive. His results are equivalent to 5–15 micrograms of barium per tube.

The greater amounts found in our experiments we believe to indicate an increased retention, which may be adsorption upon or alloying with the finely divided nickel, and which may also be a factor in a very long useful life obtained with this type of coating. The contrary opinion, that barium is dissolved in barium oxide, has some support from the work of Schriel,[14] who reports a slight solubility, though no evidence for solution under vacuum conditions. From the overall composition, as shown in Table V, we conclude that the active metal is somehow dissolved, a conclusion further substantiated by the long time, upward of two hours, necessary to leach out the active metal in the carbon dioxide treatments.

TABLE V

Coating composition (referred to outside surface of coating)

SrO = 984 μ g./sq. cm.
BaO = 923 μ g./sq. cm.
Ni = 71.5 μ g./sq. cm.
Active metal = 0.6 – 65 μ g./sq. cm. as Ba

Summary

Using a filament coated with a colloidal mixture of barium oxide, strontium oxide, finely divided nickel, and free alkaline earth metal, we have investigated the quantitative relation between thermionic emission and the content of active metal. A high level of activity was found from 15 μ g./sq. cm. to 60 μ g./sq. cm. of equivalent Ba, with a slight apparent maximum at 30 μ g./sq. cm. where the thermionic current at 1050°K. is 600 m. a./sq. cm. The electron work function is 1.37 v.

The radiant emissive power at 0.66 μ is approximately 64%, independent of the content of active metal.

The free alkaline earth metal was determined by oxidation with carbon dioxide and analysis of the gaseous reaction products,

NEW YORK, N. Y. RECEIVED AUGUST 29, 1938

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[12] T. P. Berdennikowa, *Phys. Z. Sowjet.*, **2**, 77 (1932).

[13] H. Fritz, *Mikrochemie*, **17**, 191 (1935).

[14] M. Schriel, *Z. anorg. Chem.*, **231**, 313 (1937).

[CONTRIBUTION FROM THE ANALYTICAL LABORATORIES OF FORDHAM UNIVERSITY]

A Modified Method for the Preparation of Monochloropentamminocobaltic Chloride (Purpureocobaltic Chloride)

BY WALTER A. HYNES, LEO K. YANOWSKI AND MORRIS SHILLER

Monochloropentamminocobaltic chloride, or purpureocobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, is one of the earliest and best-known of the cobaltammines. During the course of work on the application of such complexes to the microscopic detection of anions,[1] it became necessary to prepare relatively large amounts of this substance in a pure state.

Purpureocobaltic chloride has been prepared and its constitution studied by numerous investigators[2] since its initial synthesis in 1851. These workers used air or pure oxygen as chief oxidants and cobaltous carbonate as the usual source of cobalt.

The chief objections to the older method of preparation are the length of time required for the preparation of the substance, the low yield of pure substance obtained and the impurity of the final product. The low yield and relative impurity of the final product obtained by the usual method are due to the presence of hexammines and other cobaltammines, only removable by repeated recrystallizations or by precipitation from cold

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[1] W. Hynes and L. Yanowski, *Mikrochemie*, **23**, 1, 143 (1937).

[2] "Gmelins Handbuch der anorganischen Chemie," 8 Aufl., 58B, Berlin, 1930, pp. 151–159.