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Studies on the Mechanism of Operation of the L Cathode. II

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An experimental study of the L cathode is presented, including the chemistry of carbonate decomposition and barium generation, the origin of BaO in the evaporant, the barium transport mechanism through the porous plug, and the factors determining cathode life. Carbonate decomposition is accompanied in low porosity cathodes by the deleterious reaction

$BaCO_3 + \frac{1}{3}W = \frac{1}{3}Ba_3WO_6 + CO.$

Barium is generated in the cavity at an equilibrium pressure by the reaction

 $2BaO + \frac{1}{3}W = \frac{1}{3}Ba_3WO_6 + Ba$

and is transported continuously through the porous tungsten predominantly by Knudsen flow. During transport the barium acquires oxygen from the tungsten, producing in the evaporant a large BaO content which helps to activate the surface. Termination of life coincides with completion of the BaO-W reaction and onset of the subsequent reaction

$$\frac{2}{3}Ba_3WO_6+\frac{1}{3}W=BaWO_4+Ba,$$

which is accompanied by release of a poisoning agent. Material decrease in evaporation rate and a corresponding increase in cathode life may be gained by addition of SrCO₃.

I. INTRODUCTION

 \mathbf{I}^{N} Part I¹ it was shown that the work function of the tungsten surface of an L cathode is lowered by a dipole layer of oxygen and barium. It is the purpose of this part to deal with the formation of the barium and barium oxide required to activate the cathode, their transport to the surface, the factors determining cathode life, and the role of strontium.

II. CHEMICAL PROCESSES DURING CARBONATE BREAKDOWN

The reaction desired during carbonate breakdown is thermal decomposition in accordance with

$$BaCO_3(s) = BaO(s) + CO_2(g).$$
(1)

For this reaction the equilibrium pressure of carbon dioxide is given by²

$$\log P(\rm{mm}) = -13075/T + 10.549.$$
(2)

For a typical breakdown temperature of 1000°C the equilibrium pressure is sufficiently high (1.8 mm) so that the decomposition rate may be expected to be limited only by the gas removal rate. Unfortunately, tungsten is susceptible to oxidation by carbon dioxide and the following side reaction can occur³:

$$\operatorname{BaCO}_{3}(s) = \frac{1}{3}\operatorname{W}(s) = \frac{1}{3}\operatorname{Ba}_{3}\operatorname{WO}_{6}(s) + \operatorname{CO}(g). \quad (3)$$

For this case the equilibrium pressure of carbon monox-

ide has been estimated thermochemically^{4,5} to be

$$\log P(\rm{mm}) = -8700/T + 11.90. \tag{4}$$

At 1000°C this pressure is ca 10⁵ mm; hence, reaction (3) is thermodynamically highly favorable. Indeed, an intimate mixture of barium carbonate and tungsten may so react quantitatively.³ Since reaction (3) wastes barium carbonate, it is necessary to minimize it relative to reaction (1).

To determine the conditions which favor reaction (1) and to identify the reactions occurring during breakdown, 5 cathodes (porosity = 28%, BaCO₃, filling) were subjected to breakdown with varying speeds and the residual material in the cavities and on the bottom of the tungsten bodies examined by x-ray diffraction. The results (Table I) indicate the main reactions during breakdown to be indeed (1) and (3), and they underline the importance of slow breakdown to obtain barium

TABLE I. Reaction products for varying breakdown speeds.

Cathode No.	Breakdown temp. °C	Breakdown time, min.	Ambient pressure, mm	Major constituent of reaction products
1	945	1440	<3×10 ⁻⁷	BaO
2	1000-1010	130	<10-5	BaO
3ª	1020	4	<10-4	Ba ₃ WO ₆
4ª	1020-1125	3	>10-4	Ba ₃ WO ₆
5ª	1010-1310	1	≫10⁻₄	Ba ₃ WO ₆

Cavity empty after breakdown, reaction products adhering to bottom of W plug.

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^{*} Present address: Mead Research Laboratories, Chillicothe,

Ohio. ¹ Rittner, Ahlert, and Rutledge, J. Appl. Phys. 28, 156 (1957),

² J. J. Lander, J. Am. Chem. Soc. 73, 5794 (1951).

³ Hughes, Coppola, and Evans, J. Appl. Phys. 23, 635 (1952).

⁴ E. S. Rittner, Philips Research Repts. 8, 184 (1953).

⁵ In reference 4 the small (then unknown) heat of formation of Ba_3WO_6 from $2BaO+BaWO_4$ has been neglected. With the use of the barium pressures reported in Sec. V, this quantity has been computed to be -2.1 kcal and minor corrections to the thermochemical estimates have been based upon this result.

oxide as principal product. The maximum safe breakdown temperature, ca 1015°C, nearly coincides with the eutectic temperature, 1030°C, in the BaO-BaCO₃ system.⁶ Formation of a liquid phase, which could be drawn into intimate contact with the tungsten by capillary action, would highly favor reaction (3) and would account for an empty cavity after rapid breakdown.

III. BARIUM GENERATION

Whether the free barium in the activating stream arises from reduction of barium oxide by the tungsten plug or by the surrounding molybdenum walls may be settled by a thermochemical estimate of the equilibrium pressures of barium produced by the reactions

$$2 \operatorname{BaO}(s) + \frac{1}{3} \operatorname{W}(s) = \frac{1}{3} \operatorname{Ba}_3 \operatorname{WO}_6(s) + \operatorname{Ba}(g),$$
 (5)

$$2 \operatorname{BaO}(s) + \frac{1}{3} \operatorname{Mo}(s) = \frac{1}{3} \operatorname{Ba_3MoO_6}(s) + \operatorname{Ba}(g).$$
 (6)

The results are 4.5.7 for reaction (5):

$$\log P(\rm{mm}) = -17\ 200/T + 8.56, \tag{7}$$

and for reaction (6):

$$\log P(\rm{mm}) = -19\,600/T + 8.56.$$
(8)

The barium pressure attending reaction (5), although only 10⁻⁶ to 10⁻³ mm at cathode temperatures, is two orders of magnitude higher than that attending reaction (6). Therefore, reaction (6) will be completely repressed and the active reducing agent will be tungsten. In agreement with this conclusion, after termination of life the molybdenum walls of the cavity are found to be still bright and shiny. Further evidence that Eq. (5) represents the main reaction during cathode life comes from x-ray examination of the constituents on the bottom of the tungsten after the end of life; the major product is indeed Ba₃WO₆.

The equilibrium pressure of barium produced by reduction of barium oxide by tungsten [Eq. (7)] is also nearly two orders of magnitude higher than the vapor pressure of barium oxide, given by⁸

$$\log P(\mathrm{mm}) = -19\,700/T + 8.87. \tag{9}$$

If there were no direct contact between the solid reactants, the equilibrium pressure (7) could not be established unless the vaporization rate of the oxide onto tungsten exceeded the rate of barium loss from the cathode. This requires the transmission coefficient of the porous plug for barium to be less than the BaO/Ba pressure ratio. The latter condition is fulfilled in practice (see Sec. V), permitting establishment in the cavity of the equilibrium pressure of barium, even in the absence of reactant contact.

⁶ J. J. Lander, J. Am. Chem. Soc. 73, 5893 (1954). ⁷ The heat of formation of Ba₃MoO₆ from 2 BaO+BaMoO₄ has been assumed identical to the corresponding case for tungsten.

The completion of reaction (5) does not represent the end point in the reduction of barium oxide by tungsten since the basic tungstate is capable of further reaction with tungsten, viz.

$$\frac{2}{3}$$
 Ba₃WO₆(s)+ $\frac{1}{3}$ W(s)=BaWO₄(s)+Ba(g). (10)

Barium evolution accompanying this reaction was readily detected, and the evaporation rate at 1250°C was determined from chemical analysis of the evaporant collected over a measured interval from an L cathode filled initially with Ba₃WO₆. The average evaporation rate was about half that corresponding to reaction (5). X-ray examination of the tungsten after prolonged heating of an L cathode until cessation of barium evolution revealed that the final reaction product was indeed BaWO₄. These results refute the conclusion of reference 3 that Ba₃WO₆ is stable in contact with tungsten up to 1350°C.

Chemical studies of the amount of barium produced by reactions (5) and (10) are reported in Sec. VI.

IV. ORIGIN OF BaO IN EVAPORANT

In view of the high equilibrium ratio of Ba/BaO in the cavity, the evaporant from an L cathode might be expected to be predominantly free barium. However, as shown in Part I¹, the evaporant consists of nearly half BaO.

A hint as to the origin of this large BaO content was first supplied by analysis of the evaporant from a cathode with an accidental leak in the W-Mo weld through which practically all the barium had escaped. In this case the reducing power was in good agreement with the total barium content. This suggests that the oxide results from passage of barium through the tungsten plug. To test this hypothesis, a weighed quantity of barium azide was introduced into an L cathode structure with an enlarged cavity, the azide converted to metal, all of the latter passed through the tungsten plug, and the evaporant analyzed for total barium and reducing power. Results are summarized in Table II; in the absence of the plug no BaO was detected in the evaporant. These results indicate that the tungsten contains oxygen (0.13%) by weight) which combines with barium during passage through the plug. The excellent agreement between the quantity of barium expected in the evaporant and that found implies that no barium gets locked in the plug owing to reaction with tungsten oxide.

TABLE II. Analyses of evaporant resulting from barium flow through porous tungsten plugs. (Weight of plug, 75 mg; T = 1010 °C.)

BaNs	Ba	Total Ba found, mg		Free Ba	BaO content of
introduced, mg	expected, mg	Acidim- etrically	Polar- ographically	found, mg	evaporant, mg
9.9	6.1	6.0	6.1	5.2	1.0
3.6	2.2	2.12	2.18	1.32	0.9

⁸ O. Kubaschewski and E. L. L. Evans, Metallurgical Thermochemistry (John Wiley and Sons, Inc., New York, 1956), second edition.

The normal filling of an L cathode yields less barium via reactions (1) and (5) than is required to reduce all of the tungsten oxide. Hence, barium oxide should be present in the evaporant throughout cathode life,⁹ and the emission should not gradually diminish owing to depletion of oxygen in the dipole layer. Both deductions are consistent with observation.¹

V. BARIUM TRANSPORT MECHANISM

There are two possible means for transporting barium through the tungsten plug: by migration of barium adatoms over internal pore surfaces, and by vapor flow through the pores. Since the estimated barium pressure in the cavity [Eq. (7)] is so low that the mean free path is large compared to the pore diameter, the vapor flow component will be of the Knudsen type. Although both flow processes are in general interdependent, they become independent to a good approximation for complete coverage of all tungsten surfaces with barium, as occurs in the L cathode.¹ Moreover, in view of this high coverage the gradient in adatom concentration along the pores must be very small, leading one to expect surface migration to be unimportant relative to vapor flow.

To determine the dominant transport mechanism, measurements have been made of the rate of Knudsen flow of an inert gas through tungsten plugs of varying porosities. From these data and the estimated barium pressure in the cavity it is possible to compute the Knudsen flow component and to compare it with the cathode evaporation rate.¹ Agreement between these quantities should indicate proof of dominance of Knudsen flow.

Consider a porous plug of cross-sectional area A with one side maintained at negligible pressure and the other connected to an isolated volume V containing a gas of molecular weight M at pressure P and temperature $T^{\circ}K$. The mass rate of Knudsen flow through the plug is given by

$$\frac{dm}{dt} = -\frac{\alpha A M^{\frac{1}{2}} P}{N_A (2\pi m_0 kT)^{\frac{1}{2}}},\tag{11}$$

where α is the transmission coefficient (ratio of number of particles emerging/sec from top of plug to that impinging/sec on bottom), N_A is Avogadro's number, m_0 is the mass associated with unit atomic weight, and k is Boltzmann's constant. As gas is pumped from the reservoir through the plug, the pressure declines with time. At the low pressures in question the gas will obey the perfect gas law, which together with Eq. (11) leads to

$$P = P_0 e^{-\lambda t}, \tag{12}$$

where

$$\lambda = \frac{\alpha A (kT)^{\frac{1}{2}}}{V(2\pi m_0 M)^{\frac{1}{2}}} \tag{13}$$

and P_0 represents the initial pressure. Thus, measurement of the decay constant λ determines the transmission coefficient α . Equation (11) may then be evaluated for the steady state Knudsen flow rate of barium by employing for P the estimated pressure (7), for Mthe atomic weight of barium,¹⁰ and for T the cathode operating temperature.

To determine λ , the tungsten plug was welded to a molybdenum cylinder and the cylindrical sides of the plug polished to close the pores (as in the Ba evaporation studies¹) to confine emergence of gas to the top surface. This assembly was connected via a wax seal to a calibrated volume of either helium or nitrogen, the pressure of which was monitored by a Pirani gauge. Finally, the top side of the plug was maintained at negligible pressure by a kinetic vacuum system and the pressure in the calibrated volume measured vs time. The choice of initial pressure ensured that the mean free path exceeded the pore diameter at all times. The observed decrease in pressure with time proved to be accurately exponential. To check the magnitude of the decay constant, flow rates of both nitrogen and helium through a long length of calibrated capillary glass tubing were measured and found to agree with expectation.

Results for α obtained on 17 tungsten plugs¹¹ of varying porosity are shown in Fig. 1. The transmission coefficient is of the order of 10^{-4} , which is far smaller than the BaO/Ba equilibrium pressure ratio in the cavity. The Knudsen flow component for a highporosity plug (porosity=27%) computed from this data and Eq. (7) is shown in Fig. 2 as the dashed line A'. The observed¹ evaporation rate from a cathode of the same porosity is shown as the solid line A. The computed rate for a low porosity plug (porosity=17%) is shown as dashed line B' and the observed¹ rate as the solid line B. Finally, a similar computation for a very low porosity plug (porosity=12.2%) is shown as line

⁹ D. L. Schaeffer and J. E. White [J. Appl. Phys. 23, 669 (1952)] have concluded that the evaporant consists only of barium metal, based upon comparison of the work function of a precleaned tungsten wire covered with a monolayer or a multiatomic layer of evaporant (ϕ_0 =1.58, 2.02 ev, respectively) with literature values [A. L. Reimann, *Thermionic Emission* (Chapman and Hall, Ltd., London, 1934)] for a Ba-W surface (1.58 ev) and for bulk barium (2.11 ev). However, the literature cited is somewhat old and the values differ materially from the more recent ones: 2.15 ev for Ba-W¹ and 2.51 ev for bulk barium [G. Hermann and S. Wagener, *The Oxide-Coaled Calhode* (Chapman and Hall, Ltd., London, 1951), Vol. II, p. 98].

¹⁰ The oxygen content of the evaporant should strictly be included in M. However, the mass rate of Knudsen flow for pure BaO is higher by only 6%. Since the emerging stream is only about half BaO and since Ba traverses a significant (unknown) fraction of its total path as atoms before acquiring oxygen, the error introduced from the use of M_{Ba} is negligible.

error introduced from the use of M_{Ba} is negligible. ¹¹ The plugs were prepared by pressing tungsten powder in a die and sintering at a high temperature in hydrogen. The porosity was varied by altering the pressure, temperature, and firing time. The relationship shown in Fig. 1 is not universal since α is not a single-valued function of porosity but depends more fundamentally upon the number and size of the pores.

(15)

C' superposed upon one experimental point (open circle). In all cases the Knudsen flow rate is in excellent agreement with the observed evaporation rate. Also, the evaporation activation energy, 3.25 ev (determined from the slope of line A),¹² is in good agreement with the enthalpy change accompanying reaction (5), e.g., 3.40 ev. Hence, we conclude that Knudsen flow dominates transport and evaporation processes13 and that the equilibrium pressure of barium is indeed established in the cavity. The pressure may now be determined from the observed values of evaporation rate and transmission coefficient. For reaction (5) we get

$$\log P(\mathrm{mm}) = -16\,400/T + 8.02,\tag{14}$$

which differs only slightly from the estimated pressure (7). For reaction (10) we obtain

 $\log P(mm) = -16\,860/T + 8.02$.



FIG. 1. Transmission coefficient vs porosity of tungsten plug. Diameter = 3.4 mm, thickness = 0.5 mm, sides polished.

Further confirmation that Knudsen flow is dominant comes from measurements1 of the minimum arrival rate of Ba+BaO necessary to keep a well-activated tungsten surface completely covered; these data are replotted in Fig. 2 as curve D. Since in dynamical equilibrium the arrival rate will just balance the evaporation rate, D represents the adatom evaporation



FIG. 2. Evaporation rate of barium vs temperature and porosity. experimental, high porosity; B-experimental, low porosity; A A', B', C'—computed from Ba pressure and Knudsen flow rate; -adsorbed Ba component. D

component, which is far smaller than observed evaporation rates.

VI. CATHODE LIFE

Accelerated life tests were carried out at 1250°C as a function of cathode porosity and of the initial barium carbonate charge. Immediately after seal-off and periodically throughout emission life, measurements were made of the instantaneous total barium evaporation rate at 1250°C and of the emission density at 1190°C. The cathode was then heated further until barium evolution ceased and the evaporant analyzed



FIG. 3. Accelerated life test at 1250°C. - - - - emission density at 1190°C, -- total Ba evaporation rate, porosity =27%, filling-2.03 mg BaCO₃.

¹² The activation energy determined from the slope of line B_1 3.0 ev, is slightly lower, which might be explained as follows: If the cathode is incompletely activated, the minimum arrival rate of barium required for complete coverage may be as much as fifteen-fold higher than curve D.¹ Since the slope of D is much lower than that of A or B, the contribution of the adatom evaporation component may not be negligible relative to the Knudsen flow component in relatively fresh, low-porosity cathodes at lower temperatures, resulting in too low a slope of the single line drawn through the experimental points.

¹³ Knudsen flow was deemed unimportant by Schaeffer and White [J. Appl. Phys. 23, 669 (1952)]; however, they considered only the flow of BaO vapor, apparently not realizing that the pressure of free Ba could greatly exceed the BaO vapor pressure.

TABLE III. Dependence of activation time and emission life on plug porosity and BaCO₃ charge $(T=1250^{\circ}C)$, high porosity =27%, low porosity =17%, polished sides).

Porosity	Quantity BaCO3, mg	Activation time, hr	Emission life,* hr	Normalized life, hr/mg
High	2.03	45	210	103
High	1.90	60	190	100
High	6.60	240	720	109
Low	2.20	115	305	138
Low	6.90	320	1040	151

 Defined as time after seal-off for emission to fall to one-half maximum value.

for total barium. Typical results are displayed in Fig. 3 for a high porosity cathode. The cathode activated in 45 hr and then the emission remained constant until sudden termination of life after about 200 hr.

The dependence of activation time and cathode life on plug porosity and on initial quantity of barium carbonate is shown in Table III. The activation time decreases with porosity and increases with the barium carbonate charge. The porosity effect is to be expected because of the higher barium flow rate. The charge effect may result from passage through the plug of a larger quantity of carbon dioxide which further oxidizes the tungsten. For a given porosity the life is proportional to the quantity of barium carbonate employed. However, low-porosity plugs yield a much smaller life relative to high porosity ones than would be anticipated from their fivefold lower Knudsen flow rate. Reaction (3) may play a more profound role in this case.

Returning to Fig. 3, we note that the evaporation rate is substantially constant during cathode life. The barium oxide evaporation rate (not shown) is also constant during life and corresponds to an oxide content of 42%. For a low-porosity cathode the behavior is



FIG. 4. Emission density from L cathode at 1020°C vs arrival rate of externally supplied barium. A—after end of Ba evolution from cathode, B—after end of cathode life.

similar, but the evaporation rate is fivefold lower, in accordance with the lower Knudsen flow rate, and the oxide content somewhat higher, viz., 57%. The rapid decline in emission is accompanied by a slight drop in evaporation rate; however, barium evolution does not cease at this time. Coincident with cathode death, a peak in the evaporation rate exceeding that during emission life is observed; and then barium evolution continues at a decreasing rate for an additional time comparable to emission life. During this stage there is an increase in evaporant oxide content (to about 65% for a high-porosity cathode) and a change in physical appearance, a thick film exhibiting interference colors rather than the previously uniform gray color. These observations coupled with the complete lack of emission despite an adequately high barium arrival rate to the surface suggest that emission failure may result from internal release of oxygen or of an oxygen-bearing poisoning agent.

To test this idea, a pure barium stream from an external gun was directed onto the surface of an L cathode which had been life tested to the end of life, and measurements were made of cathode emission vs barium arrival rate (curve B, Fig. 4).¹⁴ The barium

TABLE IV. Material balance. (High porosity cathodes.)

1	2 Ba expected	Ba .	4 Ba finally	5
BaCO₃ introduced, mg	from reactions (1) and (5), mg	tound at end of life, mg	expected from reactions (1), (3), (5) and (10), mg	Ba finally found, mg
2.03 6.45	0.71 2.42	0.49 1.50	0.96 2.99	1.17 3.12

stream increased emission from zero to nearly half of the standard L cathode value at the highest arrival rate attainable. The cathode was then heated until barium evolution ceased and the experiment repeated (curve A, Fig. 4). In this case standard emission was produced at a sufficiently high arrival rate, which was lower by a factor well in excess of 5 than the rate required to achieve full emission at the end of cathode life. These observations support the notion of a poisoning agent¹⁵ released internally and requiring a large quantity of barium for neutralization. Thus, it appears that normal emission occurs so long as barium is generated by the BaO-W reaction (5) and that emission fails when the Ba_3WO_6-W reaction (10) takes over as the source of barium. In conformity with this view, an L cathode containing an initial filling of Ba_3WO_6 (prepared from 3 $BaCO_3 + WO_3$) does not

¹⁴ Measurements by R. H. Ahlert.

¹⁶ A search for the poisoning substance has been based on the hypotheses that it might consist of oxygen from thermal dissociation of BaWO₄, or of BaWO₄ reaching the emitting surface by volatilization, either of which could account in principle for the increased evaporation rate at the end of life. However, further, experiments have ruled out both possibilities, and the identity and origin of the poisoning agent still stand as major unsolved problems.

develop electron emission, although barium is generated at an average rate half that of reaction (5).

A material balance for barium (Table IV) based upon reactions (1), (3), (5), and (10) yields further evidence that these are the reactions occurring in the cathode. The quantity of barium found at the end of life (column 3) is lower than that expected (column 2) from quantitative dissociation of carbonate to oxide and complete reduction of the latter to basic tungstate, suggesting that $\frac{1}{3}$ of the barium carbonate is wasted via CO-producing reaction (3).¹⁶ (The corresponding waste in a low-porosity cathode amounts to about 80%, despite the much slower breakdown employed.) The total amount of barium found in the evaporant after cessation of barium evolution (column 5) is in reasonable agreement¹⁷ with that expected (column 4) from the reaction with tungsten of the remaining barium oxide followed by the Ba_3WO_6-W reaction, including the Ba₃WO₆ produced by reaction (3).

VII. ROLE OF STRONTIUM

It is known¹⁸ that a monolayer of barium on tungsten is far more stable and yields much higher emission than a monolayer of strontium on tungsten. The close similarity of the emission from the $BaCO_3 - SrCO_3$ -filled cathode to that of the $BaCO_3$ -filled version¹ suggests that the emitting surface is nearly identical in both cases; and the reason is undoubtedly that strontium atoms issuing from the pores do not stick to tungsten at cathode temperatures.

On the other hand, the marked increase in cathode life produced by strontium must reflect either an important change in the cathode chemistry or in the transport mechanism. To investigate these possibilities, commercial cathodes were studied containing 1.6 ± 0.1 mg of a $BaCO_3 - SrCO_3$ solid solution of 54 wt % $SrCO_3$. a filling chemically equivalent to 1.9 mg of BaCO₃. The tungsten plugs were of high porosity (24.5%), 3.1 mm in diameter, and the cylindrical sides were left unpolished. The cathodes were life tested at 1250°C until emission failure occurred, which required 2200 hours on the average. Correcting for slight differences in porosity and dimensions of these plugs relative to those studied previously, one concludes that a chemically equivalent filling containing strontium produces a fourteen-fold improvement in life.

The reducing power of the evaporant was determined

¹⁸G. E. Moore and H. W. Allison, J. Chem. Phys. 23, 1609 (1955). by the hydrogen evolution method, the total alkaline earth measured by acidimetric titration, and the barium content determined polarographically. Thus it was determined that the evaporant contained 0.23 mg of Ba and 0.24 mg of Sr with an oxide content, computed as BaO, of 50%. The Sr content of the evaporant, 62 mole% Sr, corresponds closely to the Sr content of the initial carbonate mixture, 61 mole%. If the analog of reaction (3) for the carbonate solid solution were negligible, a reasonable supposition since the plug sides were left unpolished,¹⁶ and if alkaline earth vapor were produced according to the analog of reaction (5), viz:

$$4 \operatorname{BaO} \cdot 6 \operatorname{SrO}(ss) + (5/3) \operatorname{W}(s) = \frac{2}{3} \operatorname{Ba_3WO_6} \cdot \operatorname{Sr_3WO_6}(ss) + 2 \operatorname{Ba}(g) + 3 \operatorname{Sr}(g), \quad (16)$$

then a total of 0.26 mg of Ba and 0.26 mg of Sr would be expected in the evaporant, in good agreement with the quantities found. Also, x-ray analysis of the reaction products revealed exclusively a basic tungstate phase with a lattice constant intermediate between that of Ba₃WO₆ and Sr₃WO₆. Hence reaction (16) supplies the activating material during emission life.

The chemical analyses also reveal that the average mass evaporation rate of total alkaline earth material is 1.2×10^{-6} g Ba+Sr/cm² at 1250 °C. Correcting for plug porosities and dimensions, one finds that the mass evaporation rate has been reduced in the presence of strontium by a factor of 17.5. The corresponding reduction in pressure of alkaline earth vapor in the cavity amounts to a factor of 16.

A pressure reduction of this order is understandable on thermochemical grounds. It may be shown that the equilibrium pressure of Ba+Sr vapor produced by reaction (16), P_{16} , is related to the equilibrium pressure of Ba generated by reaction (5), P_5 , and to the equilibrium pressure of Sr, P_{17} , produced by the analogous reaction,

$$2 \operatorname{SrO}(s) + \frac{1}{3} \operatorname{W}(s) = \frac{1}{3} \operatorname{Sr}_{3} \operatorname{WO}_{6}(s) + \operatorname{Sr}(g), \quad (17)$$

by the equation

$$P_{16} = 1.96 (P_5^2 P_{17}^3)^{1/5}.$$
 (18)

Here we have neglected the small free energy change attending solid solution formation and the entropy of mixing of the vapors, which we estimate might reduce P_{16} below the value (18) by a factor only slightly exceeding unity. P_5 is given by Eq. (14) while P_{17} has been determined experimentally¹⁹ to be

$$\log P(\text{atmos}) = -18\ 100/T + 2.286 + 0.5\ \log T.$$
 (19)

On evaluating these pressures at 1250°C, we find

$$P_{5}/P_{16} = 14.$$
 (20)

¹⁶ However, if the cylindrical sides of the tungsten plug are not polished to close the pores, loss of $BaCO_3$ via reaction (3) becomes negligible for a high-porosity plug. Thus, although polishing reduces the evaporation rate by a factor of about 2, the net improvement in life is only about 1.3 fold.

ⁱ⁷ However, the slight disparity of 0.1 to 0.2 mg exceeds experimental error. The origin of this extra Ba has been traced to reduction of BaWO₄ by residual impurities in the tungsten. The Ba pressure is too low, however, for these impurities to play a significant role during cathode life.

¹⁹ Moore, Allison, and Morrison, J. Chem. Phys. 18, 1579 (1950). These workers have expressed the composition of the reaction product formed in Eq. (17) as $SrWO_3$, but more recent work by Rooksby and Steward [J. Appl. Phys. 22, 358 (1951)] has shown that it is Sr_3WO_6 .

Hence, barium and strontium are present in the cavity at their equilibrium pressures²⁰ corresponding to reaction (16), and it is the lowering of the barium pressure by strontium which produces the large increase in cathode life. However, increased susceptibility to poisoning is the price paid for this improvement. Despite the pressure reduction, the partial pressure of barium is still sufficiently high so that Knudsen flow transport remains dominant (see Fig. 2).

After the end of life some tubes were heated for an additional period with a plate covering the cathode to collect additional evaporant. Subsequent acidimetric titration revealed a total of 0.26 mg of Ba and Sr in exact agreement with the amount to be expected from the reaction:

$$\frac{2}{3} \operatorname{Ba_{3}WO_{6}} \cdot \operatorname{Sr_{3}WO_{6}}(ss) + \frac{5}{6} W(s) = \operatorname{BaWO_{4}} \cdot \frac{3}{2} \operatorname{SrWO_{4}}(ss) + \operatorname{Ba}(g) + \frac{3}{2} \operatorname{Sr}(g).$$
(21)

X-ray examination revealed the end product on the plug to be a solid solution of $BaWO_4$ and $SrWO_4$. Thus, end of life coincides with the onset of a reaction analogous to (10) and is presumably caused by the accompanying release of a poisoning agent.

There is also a technical advantage accruing from the use of $BaCO_3$ -SrCO₃. Since SrCO₃ tends to dissociate more readily than $BaCO_3$ and since a low melting eutectic in the system BaO-SrO-CO₂ does not occur, breakdown can be carried out more readily with less danger of premature cathode failure owing to wastage of the reservoir via CO production.

VIII. CONCLUSIONS

Breakdown of a $BaCO_3$ -filled cathode must be carried out below the eutectic temperature in the $BaO-BaCO_3$ system and as slowly as feasible to minimize the wasteful reaction

$$BaCO_3 + \frac{1}{3}W = \frac{1}{3}Ba_3WO_6 + CO.$$

The importance of this reaction decreases with tungsten porosity.

The barium necessary to activate the cathode and to maintain the monolayer during life is generated by the reaction

$$2 \text{ BaO} + \frac{1}{3} \text{ W} = \frac{1}{3} \text{ Ba}_{3} \text{WO}_{6} + \text{Ba}_{3}$$

at an equilibrium pressure given by

$$\log P(\mathrm{mm}) = -16\,400/T + 8.02,$$

in good agreement with the pressure estimated thermochemically.

The barium is transported through the porous tungsten predominantly by Knudsen flow of the vapor, which process accounts for the observed dependence of evaporation rate on porosity. During passage through the plug, nearly half of the barium picks up oxygen from the superficially oxidized tungsten.

Termination of life coincides with the completion of the BaO-W reaction and with the onset of the subsequent reaction:

$$\frac{2}{3}$$
 Ba₃WO₆+ $\frac{1}{3}$ W = BaWO₄+Ba,

because the latter is accompanied by release of an oxygen-bearing poisoning agent.

Reactions in the $BaCO_3$ -SrCO₃-filled cathode are completely analogous; however, the presence of strontium produces a substantial reduction in barium pressure which leads to a corresponding lengthening of life. A subsidiary advantage is greater ease of carbonate breakdown.

We may now appraise the possibility of improving cathode performance. While the emission is close to the maximum that can be expected, the evaporation rate of the BaCO₃-filled cathode is unduly high and the life correspondingly short owing to the excessively rapid Knudsen flow rate. Improvement in both quantities may be obtained by reducing the plug porosity and/or by reducing the barium pressure by chemical means. Significant improvement by porosity reduction, however, requires the use of a starting material other than the carbonate, which would avoid deleterious reactions similar to (3). As already noted, one successful method of improving life by chemical means is the introduction of SrCO₃. Although the resulting barium evaporation rate is still substantially higher than the minimum consistent with full emission, an unexploited degree of freedom resides in the choice of the SrCO₃/ BaCO₃ ratio. However, practical considerations of activation time and of recoverability from poisoning may limit the ultimate degree of improvement in evaporation rate and life that can be achieved by increasing this ratio.

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 $^{^{20}}$ However, during the first 25 hr of life the instantaneous evaporation rate is substantially higher than the average value and declines rapidly with time, possibly because of incomplete solid solution formation in the oxides immediately after breakdown.