

## The Vapor Pressure and Rate of Evaporation of Barium Oxide

J. P. Blewett, H. A. Liebhafsky, and E. F. Hennelly

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dioxide found. There remains a pressure increase that is unaccounted for. It is surprising and probably significant that this pressure change is quite nearly the same as the quantity of condensed material unaccounted for. Certain it is, however, that from this and the quantities of reactants and volatile products, there is in accordance with the proposed mechanism, no change in the numbers of molecules during reaction.

It does not seem that the suggestion made by Echols and Pease<sup>2</sup> of an equilibrium between methyl, nitric oxide and the complex is applicable in this case to account for the low ratios of nitric oxide to azomethane disappearing. Rather would decomposition of the complex to form two molecules, one condensible and the other reacting analytically the same as nitric oxide seem to fit the results of Experiments 16, 7 and 19. This would lead approximately to the experimental values of the pressure increase and condensed product not accounted for. This explanation

would not apply in those cases where the ratio is greater than two where the unaccounted-for quantities are still of the same magnitude. The situation is evidently too complex to admit of a simple yet complete explanation.

It nevertheless appears certain that the energies of activation of the disappearance of azomethane alone and in presence of nitric oxide are the same and that probably therefore the rate-controlling step is the same for both. It seems reasonable that this involves the production of a methyl radical. Although the principle of microscopic reversibility would favor a dissociation into two radicals rather than three, Rice and Gershinowitz<sup>6</sup> have given reasons for belief that the latter occurs, that is, both methyl radicals are formed in a single act together with nitrogen. In any event the radical  $\text{CH}_3-\text{N}=\text{N}-$  would be very unstable and thus rapidly eliminate nitrogen.

<sup>6</sup> Rice and Gershinowitz, *J. Chem. Phys.* **3**, 479 (1935).

## The Vapor Pressure and Rate of Evaporation of Barium Oxide

J. P. BLEWETT, H. A. LIEBHAFSKY AND E. F. HENNELLY

*Research Laboratory, General Electric Company, Schenectady, New York*

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The extensive investigations of the rate of evaporation of barium oxide by Claassen and Veenemans, and Herrmann are in serious disagreement. In both sets of experiments the oxide was allowed to evaporate from an exposed surface into a vacuum, a method which in this particular case may involve large temperature uncertainties. In the hope of reducing these uncertainties, the method of Knudsen has been applied; in this method the oxide escapes through a small aperture in the wall of a "blackbody" at a rate so small that the equilibrium vapor pressure is not sensibly disturbed. The final results are in agreement with those of Claassen and Veenemans. The vapor pressure of barium oxide is given by

$$\log_{10} p(\text{mm Hg}) = 8.63 - 19,400/T(1200-1800^\circ\text{K}).$$

NUMEROUS measurements<sup>1</sup> of the rate of evaporation of barium oxide have been inspired by its importance in the construction of oxide-coated cathodes. It is found, in general, that a cathode coated with barium oxide, either

pure or mixed with other alkaline earth oxides, depends for its activity on barium liberated from the barium oxide. Consequently, the cathode is no longer active when the barium oxide has completely evaporated. Until the appearance of the recent work of Herrmann,<sup>2</sup> the rate of evaporation of barium oxide, both from pure barium oxide and from solid solutions

<sup>1</sup> H. D. Arnold, *Phys. Rev.* **16**, 70 (1920); M. D. Thompson and W. G. Armstrong, *Trans. Am. Chem. Soc.* **54**, 85 (1928); Reerink (cf. Zwikker, *Physica* **8**, 241 (1928)); A. Claassen and C. F. Veenemans, *Zeits. f. Physik* **80**, 342 (1933).

<sup>2</sup> G. Herrmann, *Zeits. f. physik. Chemie* **35B**, 298 (1937).

with strontium oxide or calcium oxide, was considered to have been established by the work of Claassen and Veenemans. Herrmann, however, published a complete and self-consistent set of observations agreeing with those of Claassen and Veenemans only around 1400°K. Above and below this temperature the experimental curves diverge, Herrmann's corresponding to a heat of sublimation of 119 kcal., whereas Claassen and Veenemans' curve yields a heat of only 90 kcal. As a result, Herrmann's curve indicates a rate of evaporation lower by a factor of ten than the rate given by Claassen and Veenemans for the temperature range around 1100°K, in which most oxide-coated cathodes are operated.

Both of these investigations involved variations of Langmuir's method of vapor pressure measurement; the oxide evaporated from an oxide surface directly into a vacuum. In both cases the oxide was coated on a metal surface. When this metal was heated, oxide evaporated onto a neighboring collector.

In applying this technique to coatings of low thermal conductivity it is very difficult to estimate the temperature at the place where evaporation is taking place. The emissivity of oxide coatings cannot be predicted, so direct pyrometer measurements are impossible. The thermal conductivity of barium oxide is so low that at 1400°K gradients of 100° are possible in a coating 200 $\mu$  thick. Finally, it is difficult to decide precisely where the evaporated oxide originated, since barium oxide coatings are usually porous and cracked. If thermal gradients exist, the major part of the evaporated deposit could have come from crevices which penetrated to a hotter region of the oxide.

The method of Claassen and Veenemans is illustrated by Fig. 1. When the platinum cylinder was heated by high frequency induction, oxide evaporated from its inner surface onto the outer surface of a coaxial quartz tube filled with liquid air. The temperature of the outside of the platinum cylinder, obtained by pyrometer measurements, was assumed to be the temperature of the oxide surface. The correctness of this assumption is difficult to prove. Between the platinum and the liquid air there existed a temperature difference greater than 1200°, which must have

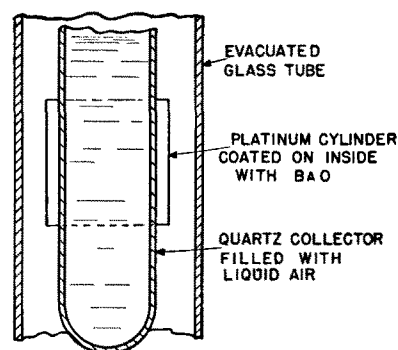


FIG. 1.

been the sum of the temperature gradients in the oxide coating, in the intervening vacuum, and in the quartz. A calculation would involve several unknown quantities (for instance, the thermal conductivity and emissivity of barium oxide), and is further complicated by the geometry of the apparatus. It is true, however, that a concave surface permits a closer approach to blackbody conditions than does a plane or a convex surface. Also, the effect of evaporation from cracks was to compensate for errors in estimation of the oxide surface temperature, since the temperature at the base of a crack would be more nearly the temperature of the platinum support.

More serious objections apply to the method of Herrmann. In his experiments the oxide was evaporated from the outside of a metal cylinder heated internally by radiation. To determine the true surface temperature of the oxide, he made pyrometer measurements on small spots of chromium oxide deposited on the surface. The spectral emissivity ( $\lambda=0.665\mu$ ) of chromium oxide is known to be about 0.8 over the temperature range involved, so that measurements of brightness temperature permit a deduction of its true temperature. Unfortunately, the temperature of the chromium oxide is not necessarily that of the neighboring barium oxide, since the spot cools itself by radiation at a different rate than does the barium oxide. Liebmann,<sup>3</sup> to whom Herrmann refers, emphasizes the fact that this method is valid only if a series of measurements is made on spots of different areas and the curve of temperature against spot area is extrapolated to zero area. In the work of

<sup>3</sup> G. Liebmann, *Zeits. f. Physik* **63**, 404 (1930).

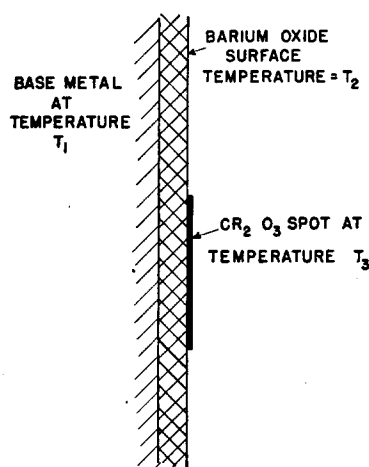


FIG. 2.

Herrmann this does not appear to have been done. From the photograph of his tube it is evident that the diameter of the spots which he used was considerably greater than the thickness of the oxide coating. Consequently the direction of the flow of heat was outward from the core metal to the surface rather than along the surface. If  $T_1$  is the true temperature of the base metal,  $T_2$  the true temperature of the barium oxide surface, and  $T_3$  the true temperature of the chromium oxide surface (see Fig. 2), we can equate the quantity of heat arriving by conduction at the outer surface, to the quantity of heat radiated by the outer surface to obtain:

$$\begin{aligned} \frac{k}{d}(T_1 - T_2) &= e_{\text{BaO}} \sigma T_2^4, \\ \frac{k}{d}(T_1 - T_3) &= e_{\text{Cr}_2\text{O}_3} \sigma T_3^4, \end{aligned} \quad (1)$$

where  $k$  = thermal conductivity of BaO,  $d$  = thickness of coating,  $e_{\text{BaO}}$  and  $e_{\text{Cr}_2\text{O}_3}$  = total emissivities of BaO and  $\text{Cr}_2\text{O}_3$ ,  $\sigma$  = Stefan's constant.

Sufficient experimental data are not available for an exact calculation of the difference between  $T_2$  and  $T_3$ . It is possible, however, to estimate the order of magnitude of this difference with the aid of a few reasonable assumptions.  $k^4$ ,  $^5$  is probably of the order of  $3 \times 10^{-4}$  cal./grad/cm<sup>2</sup>/sec. =  $1.3 \times 10^4$  ergs/grad/cm<sup>2</sup>/sec.  $d$  in Herr-

<sup>4</sup> P. Clausning and J. B. Ludwig, *Physica* **13**, 193 (1933).

<sup>5</sup> E. Patai and Z. Tomaschek, *Kolloid Zeits.* **74**, 253 (1936).

mann's experiments was between 150 and 200 $\mu$ .  $e_{\text{BaO}}$  and  $e_{\text{Cr}_2\text{O}_3}$  are not known, but if we assume  $e_{\text{BaO}} = 0.35$  (cf. reference 4) and  $e_{\text{Cr}_2\text{O}_3} = 0.8$ , we find, on solving Eqs. (1), that  $T_2$  and  $T_3$  may differ by as much as 100° in the temperature range in which Herrmann made his measurements.

Errors like these often increase with temperature in such a manner as not to cause obvious deviations from a straight line relation between log of vapor pressure and reciprocal temperature.

Since these considerations do not permit an unequivocal decision between the two sets of experiments, further work was undertaken. Evidently it is desirable to maintain the complete body of the oxide from which evaporation takes place at a uniform temperature. With this in view the Knudsen method was employed. In this method the evaporating substance is enclosed in a "blackbody" in which the equilibrium vapor pressure is sensibly maintained. The magnitude of this pressure is determined by measuring the rate at which the substance escapes through a small orifice. If  $m$  is the rate of evaporation in g per sq. cm per sec. from this hole, the vapor pressure can be deduced from the kinetic theory relation:

$$p = m(2\pi RT/M)^{1/2}, \quad (2)$$

where  $M$  is the molecular weight of the substance. In general the vapor pressure obeys approximately a relation of the form:

$$\log_{10} p = A - B/T. \quad (3)$$

The heat of sublimation  $Q$  can be deduced from  $B$ , since

$$Q = 2.303RB. \quad (4)$$

Thus  $m$  will obey the relation

$$\log_{10} m \sqrt{T} = A' - B'/T. \quad (5)$$

Experimental observations usually conform equally well to an equation of the more convenient form

$$\log_{10} m = A'' - B'/T. \quad (6)$$

#### METHOD I

In the first set of experiments the oxide was contained in a covered platinum crucible heated by high frequency induction. The dimensions of

this crucible were as follows:

Top diameter = 12 mm  
 Bottom diameter = 9 mm  
 Depth = 14 mm.

The platinum lid was recessed to fit closely. In the center of this lid was a circular hole 93 mils in diameter (0.044 sq. cm in area). Thus the area of the hole was less than one percent of the total area of the crucible walls.

#### TEMPERATURE SCALE

Temperatures were determined by sighting a pyrometer directly on the oxide surface through the hole in the crucible lid. Unfortunately the method of heating did not give a temperature that was uniform over the crucible and lid. The lid (except for its outer edge) was always at a lower temperature than were the side walls of the crucible, so that the surface of the charge must have attained an intermediate temperature. The light which reached the pyrometer was a mixture of light radiated by the charge and light reflected by the charge. Since the reflected light came partly from a cooler surface (the lid) and partly from a hotter surface (the crucible wall), the temperature errors which it introduced tended to compensate. A calculation performed by Mr. Frank Benford, of this laboratory, indicates that the surface temperature of the charge probably corresponded within  $10^\circ$  to the temperature measured by the pyrometer. The details of this calculation appear in a paper by Mr. Benford in the *Journal of the Optical Society of America*.

At the lower temperatures the surface temperature of the charge approached that of the crucible; at higher temperatures it approached that of the lid which was sometimes as much as  $80^\circ$  cooler than the crucible.

#### ANALYTICAL METHODS

A charge of about 200 mg of C.P. barium carbonate or C.P. barium hydroxide was heated slowly in the crucible in vacuum until decomposition to barium oxide was complete. The temperature was then raised to the evaporating temperature which was maintained in different

experiments for periods varying from fifteen minutes to one hour. The oxide which escaped through the hole in the crucible lid was completely collected on the inside surface of an inverted Pyrex glass beaker. The material on the collector was dissolved in warm hydrochloric acid. Barium sulfate was precipitated from the acid solutions in small test tubes that were allowed to digest on the steam bath to ensure complete precipitation. These test tubes were then centrifuged, the supernatant liquid carefully removed with a dropper, and the precipitate transferred to a small platinum crucible with the aid of a dropper and added water. The water in the crucible was then evaporated, the crucible ignited, and the precipitate treated with a drop of 1 : 1 sulfuric acid, which was fumed off before the final ignition. When the precipitate was small, the ignitions were repeated until the weight was constant to within a few micrograms. The absolute error in this method was probably within 10 micrograms of barium sulfate. Since the precipitate weighed from 0.1 to 5 milligrams, this error was never greater than 10 percent.

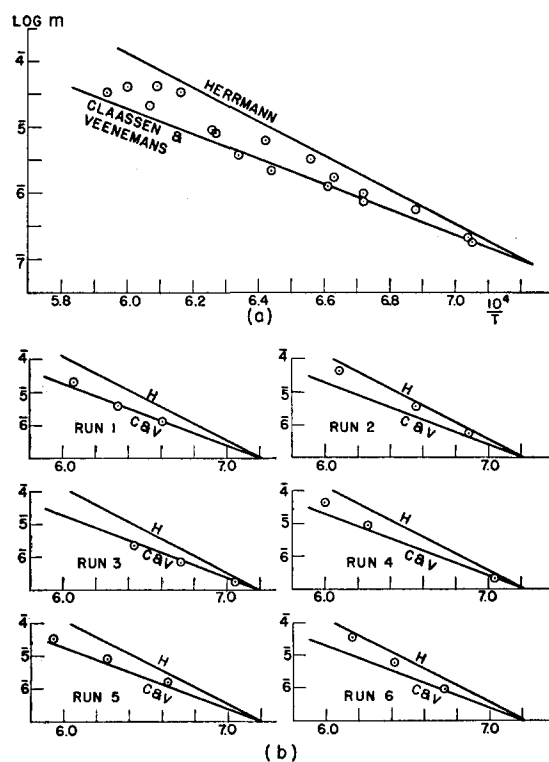


FIG. 3.

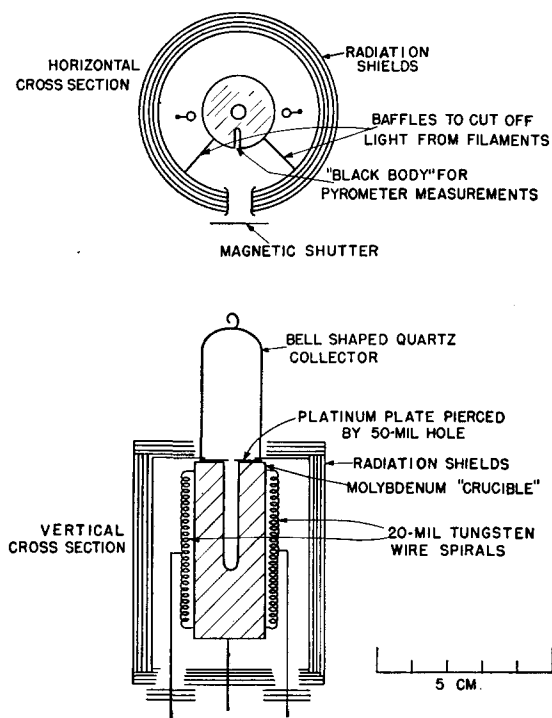


FIG. 4.

## OBSERVATIONS WITH METHOD I

Six sets of three readings each were taken on six different specimens of barium oxide: five sets on oxide produced by decomposition of barium carbonate and one (run 5) on oxide prepared from the hydroxide. When plotted together, the readings scatter considerably, as can be seen from Fig. 3(a). None, however, lies above Herrmann's curve. In Fig. 3(b) the runs are plotted separately, and it becomes evident that each run apparently defines a different straight line. This lack of agreement between the various runs is attributable to the combined effects of temperature gradients and mechanical condition of the oxide. Inspection of the charges derived from barium carbonate showed invariably that their periphery had contracted so as no longer to touch the crucible walls, and that the charges were very porous structures. Thus, depending on the fortuitous geometrical shape of the charge, it was sometimes possible for evaporation to take place from regions whose temperatures were considerably above the mean temperature given by the pyrometer. Since the temperature gradients increased with temperature, the lack of

consistency should be more marked at high temperatures, as was indeed the case.

The results obtained with barium hydroxide as the initial charge should be more significant, since this charge was found to be compact, adhering to the crucible walls, and with scarcely any visible porosity. In this case the disturbing effect of temperature gradients should be small. The readings obtained with oxide decomposed from the hydroxide agree fairly well with the curve of Claassen and Veenemans.

The results obtained by Method I seemed to indicate that the curve of Claassen and Veenemans is substantially correct. They suggest, moreover, that Herrmann's failure to corroborate it was due, not as he assumes to a variability in the heat of sublimation of barium oxide, but to uncertainties in his temperature scale and errors resulting from temperature gradients through porous coatings.

## METHOD II

It was evident that the attainment of more reliable measurements depended on the reduction of thermal gradients. With this in view, a furnace was designed as shown in Fig. 4. A hole 4 mm in diameter and 3 cm deep was drilled in a cylindrical block of molybdenum 2 cm in diameter and 5 cm long. Two 20-mil tungsten wire spirals were arc welded at both ends into holes in the block. The block was heated by passing current through these filaments, power being led in through center taps on the filaments and returning by way of a lead welded into the base of the furnace. Several closely spaced radiation shields surrounded the complete assemblage. For temperature determinations three holes 1 mm in diameter and 4 mm deep were drilled in the face of the block removed by 90° from each filament. One of these holes was in the middle of the block, the others 5 mm from either end. To prevent light from the filaments from influencing the pyrometer readings, baffles were introduced between filaments and pyrometer holes, as shown in the plan in Fig. 4. Holes were pierced in the radiation shields to permit observation of these pyrometer holes. Since a certain amount of molybdenum oxide and other impurities tended to evaporate through these holes and deposit on the tube wall,

thus tending to falsify the pyrometer readings, the holes were closed by a magnetic shutter except while readings were being taken.

With this furnace temperatures as high as 1800°K have been achieved. At this temperature the four half-filaments in parallel pass about 48 amp. The power required is about 500 watts. Pyrometer readings on the three holes at this temperature show that the temperature of the block is uniform to within 10°.

For measurements of the rate of evaporation of BaO, the molybdenum "crucible" was lined with a close-fitting platinum liner. A platinum lid was attached to the top of the molybdenum block. Evaporation took place through a 50-mil hole (0.013 sq. cm in area), so that the area of the hole is less than one percent of the area of the inside of the crucible as in Method I.

The evaporated oxide was collected on a bell-shaped quartz collector, as shown in Fig. 4. Evaporation runs were an hour long. During each run pyrometer readings of temperature were made at least three times, and they invariably checked each other within 15°. An average temperature was deduced and an average correction of 7° was added to compensate for the imperfect transmission of the glass walls.<sup>6</sup> At the end of the run the vacuum was broken by opening a side tube through which the collector was removed. A new collector was introduced through the side tube, and the apparatus could be reevacuated within five minutes of the admission of air.

The specimens were analyzed by the same

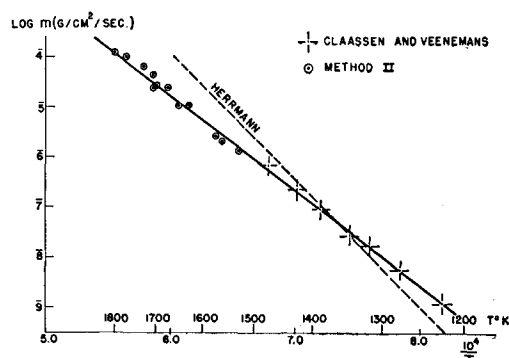


FIG. 5.

technique as was applied in connection with Method I, except that a centrifuging prior to the precipitation of barium sulfate and a washing of the precipitate were introduced in order to eliminate molybdenum impurities.

The results obtained with Method II are summarized in Table I. They are plotted in Fig. 5 together with the experimental points of Claassen and Veenemans and the line deduced by Herrmann. Our results are in good agreement with an extended line through Claassen and Veenemans' values.

In comparing our results obtained by the Knudsen method with the results of Claassen and Veenemans, who used Langmuir's method, the accommodation coefficient  $\alpha$  must also be considered, since Eq. (2) above, which connects the rate of evaporation with the vapor pressure, must be replaced for application to Langmuir's method by

$$\alpha p = m \left( \frac{2\pi RT}{M} \right)^{1/2}. \quad (2')$$

$\alpha$  has been measured for several elements and compounds,<sup>7</sup> and is usually found to be unity within the experimental error of the measurements, so that Eq. (2') reduces to Eq. (2). If the measurements of Claassen and Veenemans are accepted as correct, our agreement with their results indicates that the accommodation coefficient for barium oxide is approximately unity. We believe this to be the only information available on the accommodation coefficient of a slightly volatile oxide.

<sup>6</sup> The calculation from which this correction is deduced is outlined in a paper by Mr. Frank Benford, of this laboratory, J. Opt. Soc. Am. 29, 162 (1939).

<sup>7</sup> Cf. A. L. Marshall, R. W. Dornie and F. J. Norton, J. Am. Chem. Soc. 59, 1161 (1937).

TABLE I.

T°K	10 <sup>4</sup> T	LOG <sub>10</sub> m (G/SQ. CM/SEC.)	T (CALC. FROM EQ. (5'))	INITIAL CHARGE
1526	6.56	6.10	1517	Ba(OH) <sub>2</sub>
1561	6.40	6.30	1542	Ba(OH) <sub>2</sub>
1571	6.36	6.40	1554	Ba(OH) <sub>2</sub>
1628	6.14	5.02	1637	Ba(OH) <sub>2</sub>
1649	6.06	5.02	1637	BaCO <sub>3</sub>
1677	5.97	5.39	1690	Ba(OH) <sub>2</sub>
1700	5.88	5.41	1694	BaCO <sub>3</sub>
1707	5.86	5.39	1691	BaCO <sub>3</sub>
1707	5.86	5.63	1728	Ba(OH) <sub>2</sub>
1731	5.78	5.80	1754	Ba(OH) <sub>2</sub>
1781	5.64	4.00	1787	BaCO <sub>3</sub>
1800	5.55	4.06	1798	Ba(OH) <sub>2</sub>

With Method II the results are independent of the method of preparation of the oxide. Porous barium oxide produced by decomposition of barium carbonate and compact barium oxide derived from barium hydroxide have identical vapor pressure curves within the experimental error of our measurements.

#### PROBABLE ERRORS

Our measurements of temperature should be accurate to within 15°. The microchemical determination of weight of the deposit may introduce an error of 10 percent at the lowest temperatures. At the higher temperatures this error will be negligible. A further small source of error appears in the finite time required to raise the furnace to the evaporating temperature. Observations have been made of the rate of heating, and it is found that at the lowest temperatures the furnace may require as much as seven minutes to arrive within 10° of the desired temperature. At higher temperatures equilibrium is reached much faster. To compensate for this effect a constant correction has been added to the readings. Probably this correction is too low at the low temperatures and too high at the higher temperatures. This will result in an error of about five percent. The net result of these errors will be a mean deviation of about 25 percent. This corresponds to a mean temperature error of about 15°. As can be seen from Table I, this is about the mean

deviation of our results from the linear relation deduced below.

#### CONCLUSION

Figure 5 gives  $\log_{10} m$  (g/sq. cm/sec.) as a function of  $1/T$ . This line can be represented by

$$\log_{10} m(\text{g/sq. cm/sec.}) = 6.56$$

$$-\frac{18,900}{T}(1200-1800^\circ\text{K}). \quad (6')$$

The theoretically more precise representation

$$\log_{10} m\sqrt{T} = 8.48 - \frac{19,400}{T}(1200-1800^\circ\text{K}) \quad (5')$$

leads to the vapor pressure equation

$$\log_{10} p(\text{mm Hg}) = 8.63$$

$$-\frac{19,400}{T}(1200-1800^\circ\text{K}). \quad (3')$$

The heat of sublimation is (cf. Eq. (4)) 88,000 calories.

The good agreement which we have observed with the results of Claassen and Veenemans leads us to conclude that their temperature scale was essentially correct. There would consequently seem to be no reason for questioning the correctness of their measurements on the rate of evaporation of barium oxide from mixtures with other oxides.