or hydrogen which is in, or comes into the small volume at the front end of the tube can react directly with the mercury. We have shown that when ethylene reacts directly with the mercury it does so with an initial increase of pressure. Therefore, since at the beginning of the run we have a uniform distribution of both ethylene and hydrogen, it necessarily follows that a small amount of ethylene must react with an increase of pressure. This increase is superimposed upon the decrease due to the hydrogen reaction. This is the explanation of the small change in reaction rate after the first few minutes of each run. It now becomes evident that any increase in the reaction volume or any increase of the rate of diffusion of the ethylene into the reaction volume, must serve to emphasize such a change in rate. To test this a second set of experiments has been performed in which the reaction chamber was freed from liquid mercury. The mercury pressure was then determined by placing the globule of mercury in the trap which was kept at a temperature of 0° and an arrangement for circulating the reacting gases was introduced. These experiments, which will be reported more fully in a later paper, showed definitely an increase in the decomposition of the ethylene.

Summary

It has been shown that ethylene decomposes and polymerizes and a mixture of hydrogen and ethylene reacts to form ethane under the action of resonated atoms. The rate of ethane formation has been shown to be proportional to the square root of the hydrogen pressure. A mechanism for the reaction has been proposed and the results of other investigations have been correlated by means of the proposed mechanism.

Berkeley, California

[Contribution from the Bell Telephone Laboratories, Incorporated]

MELTING POINTS OF BARIUM, STRONTIUM AND CALCIUM OXIDES[1]

By Earle E. Schumacher

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Introduction

A search of the literature reveals the fact that there are no accurate data on the melting points of barium and strontium oxides, and but few recent data on calcium oxide. Among the earliest investigators, E. D. Clarke[2] found that barium oxide fused when heated in the oxyhydrogen

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[1] This investigation is being extended to include the binary system barium oxide-strontium oxide. Preliminary results indicate that the method described in this paper is as satisfactory for the mixtures as for the single components. The results of this work will be published at some later date.

[2] Clarke, *Ann. Phil.*, **8**, 257 (1816).

flame and Abich[3] observed that barium oxide also fused in the strongest heat of the forge. Many years later, taking advantage of the higher temperatures that could be obtained by use of the electric arc, H. Moissan[4] succeeded in melting strontium oxide to a transparent liquid at about 3273°K. and barium oxide at about 2273°K. Later Kanolt[5] made some careful observations of the melting point of calcium oxide which he determined to be 2843°K. This result has been checked by Ruff and Schmidt[6] more recently. Since during the last twenty years the technique of the production and measurement of high temperatures has made such rapid advances, the following investigation was undertaken to determine accurately by one method the melting points of all of these alkaline-earth oxides.

Method

Description.—Several methods were first tried with results not as satisfactory as anticipated, and some of these preliminary methods are described later. Since they may be of more general application, the apparatus and method with which the results reported in this paper were obtained are described immediately below. The apparatus is shown diagrammatically in Fig. 1.

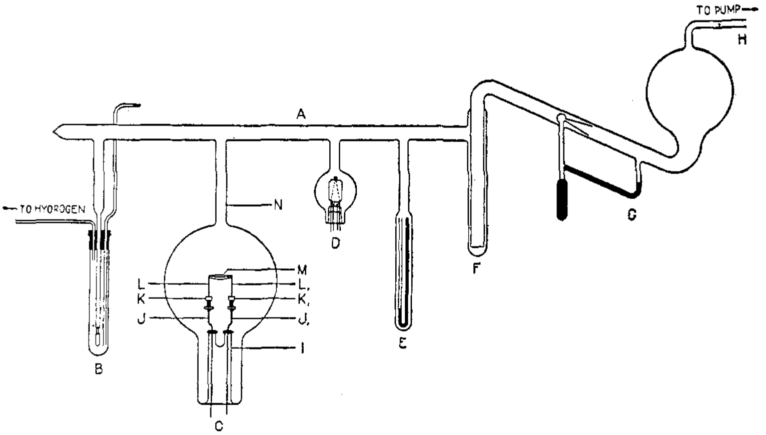

Fig. 1.—Melting-point apparatus. *A*, Glass header; *B*, Palladium valve; *C*, Melting receptacle; *D*, Ionization manometer; *E*, Mercury manometer; *F*, Liquid air trap; *G*, Mercury aspirator.

Except for the melting-point receptacle C, all parts of the apparatus may be readily reproduced by reference to the diagram.

C consisted of a glass bulb about 30 cm. in diameter into which was sealed a so-

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[3] Abich, *Pogg. Ann.*, **23**, 315 (1831).

[4] Moissan, *Compt. rend.*, **115**, 1034 (1892); **134**, 136 (1902).

[5] Kanolt, *J. Washington Acad. Sci.*, **1913**, 315–319.

[6] Ruff and Schmidt, *Z. anorg. Chem.*, **117**, 172 (1921).

called press I through which passed two heavy copper wires,[7] 0.229 cm. in diameter, J and J_1. Two molybdenum rods L and L_1, 0.290 cm. in diameter and about 7.6 cm. long, were attached to these leads by means of connectors K and K_1. The upper end of each of these rods was slotted, the slots being through the diameters and in the plane of the two rods. The width of the slots was 0.025 cm. and the vertical depth 0.508 cm. The bent ends of a strip of 0.025mm. tungsten ribbon M shaped like a boat, 0.635 cm. wide and 3.8 cm. long, were arc-welded in these slots, in an atmosphere of hydrogen, to the supports L and L_1.

Procedure.—Preliminary to a determination of the melting point of the oxide, hydrogen under atmospheric pressure was passed through the apparatus, while the boat M was heated electrically to about 1775°K. for several minutes. This reduced any tungstic oxide that might have been present on the surface of the boat. After this heating, Bulb C was cut from the header; the oxide sample, whose melting point was sought, was placed in the boat through N; C was resealed to the header A and finally the whole system was evacuated until the pressure was reduced to about 10^{-6} mm. of mercury. During the evacuation the glass walls were heated to about 675°K. to remove adsorbed gases. Upon reducing the pressure to the order of 10^{-6} mm. the apparatus was cut off from the fore pumps by a stopcock beyond H, and hydrogen was let into the apparatus through the palladium valve B, until the pressure was nearly atmospheric. Sufficient current was passed through the boat M to heat it to between 1475°K. and 1675°K. for about one minute, to reduce any tungstic oxide that might have formed on the surface of the boat after the initial heating. Enough of the hydrogen within the apparatus was then pumped out to reduce the pressure to about 0.2 atmosphere.[8] The apparatus was shut off from the pumps and current was again passed through the boat. This was very gradually increased until the boat was heated to a temperature just high enough to cause the sample within it to melt. One observer watched for this melting to occur while another followed the temperature changes of the boat very closely by means of an optical pyrometer. Temperature control of the boat and the pyrometer lamp were made very easy by placing suitable rheostats in the respective electrical circuits. The ends of the boat were, of course, cooler than the central portion, but the section of the central portion containing the sample showed very uniform temperature for a length of at least 2 cm. The

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[7] See article by W. G. Houskeeper, *J. Am. Inst. Elec. Eng.*, 5, 42, 954–960 (1923).

[8] Lower pressures were found to be unsatisfactory since, at the high temperatures attained in these experiments, the tungsten boats were found to vaporize appreciably at pressures below about 150 mm. of mercury. Pressures up to 0.5 atmosphere were used in a few experiments and the results were entirely consistent with those obtained with the lower pressures. At high pressures the heat given off by the tungsten boat M was too rapidly conducted to the walls of the glass container. Undoubtedly with a high-melting glass such as Pyrex and with adequate cooling, higher pressures could have been safely used.

temperature of the tungsten boat, at the time the sample within it melted, was taken as the melting point.

Experimental Part

Calcium Oxide.—Experiments were first conducted with calcium oxide, because of the more accurate previous knowledge of its melting point. Determinations were made on 15 different samples. Not only was Kahlbaum's c. p. calcium oxide used, but also some that was prepared in this Laboratory by decomposing chemically pure calcium carbonate.

To secure particles of suitable size to test, it was found desirable first to place the finely divided oxide in a die and press the individual particles together to form a rod. The pressure used on the die was approximately 135 atmospheres. With a jeweler's hack saw, sections of any desired shape or size were made. The dimensions of the samples used were about 1 × 0.5 × 0.5 mm. While both smaller and larger samples were used in some cases, it was found to be more difficult in these cases to obtain consistent results. Where very small samples were used it was difficult to observe accurately when the melting occurred; where very large samples were used, poor contact between the sample and the boat was frequently encountered.

It was observed that lime melted at a very definite temperature, changing abruptly from solid to liquid. This temperature was taken as the melting point of lime, for although there did seem to be a slight wetting of the tungsten by the oxide, there was no evidence of any formation of tungstate. Some determinations were made on calcium oxide that had been remelted several times in several different tungsten boats. In these experiments no change in the melting point of the lime was ever observed. The lack of a change in the melting point of the remelted samples might be explained by the absorption of impurities by the oxide only during the first melting, or the melting point being affected only by the first trace of impurities, but neither of these seems probable. Furthermore, the fact that all determinations on fresh samples gave readings very close to the average shows that if impurities were taken up during the first melt, their quantity in each case must have been the same. This, again, is not likely. The only reasonable conclusion is that no impurities affecting the melting point were taken up from the boat. The average temperature determined for the melting point of calcium oxide was 2849°K., which is in very satisfactory agreement with the value of 2843°K. obtained by Kanolt and by Ruff and Schmidt.

Barium Oxide.—The barium oxide used in the first of these experiments was prepared by decomposing pure barium carbonate, and the general melting procedure previously noted for calcium oxide was followed. All of the samples that were examined melted, solidified and

TABLE I

MELTING-POINT DATA

Source	Condition	Observed temp.,[a] °K. S_λ	Spectral emissivity e_λ	1st melt True temp., °K. T	Remelt True temp., °K. T
	CALCIUM OXIDE				
Kahlbaum	1st melt	2531	0.418	2843	..
		2531	.418	2843	..
		2537	.418	2851	..
		2531	.418	2843	..
		2531	.418	2843	..
		2537	.418	2851	..
	Remelt	2537	.418	..	2851
		2531	.418	..	2843
		2531	.418	..	2843
Calcium carbonate	1st melt	2531	.418	2843	..
		2543	.418	2858	..
		2531	.418	2843	..
		2531	.418	2843	..
		2555	.4178	2874	..
		2537	.418	2851	..
		2531	.418	2843	..
		2549	.4178	2866	..
		2537	.418	2851	..
	Remelt	2531	.418	..	2843
		2531	.418	..	2843
		2537	.418	..	2851
			Av.	2849.7	2845.7
	Melting point = 2849 °K.[b]				
	BARIUM OXIDE				
Kahlbaum	1st melt	2008	.431	2193	..
		2016	.431	2202	..
		2008	.431	2193	..
		2008	.431	2193	..
		2008	.431	2193	..
		2008	.431	2193	..
	Remelt	2008	.431	..	2193
		2016	.431	..	2202
Barium carbonate	1st melt	2008	.431	2193	..
		2008	.431	2193	..
		2023	.431	2210	..
		2008	.431	2193	..
		2008	.431	2193	..
		2008	.431	2193	..
		2016	.431	2202	..
		2008	.431	2193	..
		2016	.431	2202	..
	Remelt	2008	.431	..	2193
		2008	.431	..	2193
			Av.	2195.9	2195.3

TABLE I (*Concluded*)

Melting point = 2196 °K.[b]

Source	Condition	Observed temp., °K. S_λ	Spectral emissivity e_λ	1st melt True temp., °K. T	Remelt True temp., °K. T
	STRONTIUM OXIDE				
Kahlbaum	1st melt	2423	0.421	2705	..
		2417	.421	2698	..
		2423	.421	2705	..
		2423	.421	2705	..
		2430	.4208	2714	..
		2417	.421	2698	..
	Remelt	2423	.421	..	2705
		2423	.421	..	2705
Strontium carbonate	1st melt	2417	.421	2698	..
		2423	.421	2705	..
		2410	.4215	2688	..
		2423	.421	2705	..
		2417	.421	2698	..
		2403	.4215	2680	..
		2430	.4208	2714	..
		2430	.4208	2714	..
		2423	.421	2705	..
	Remelt	2417	.421	..	2698
		2430	.4208	..	2714
		2423	.421	..	2705
			Av.	2702.1	2705.4

Melting point = 2703 °K.[b]

[a] See paragraph entitled "Calibration of Optical Pyrometer."

[b] Average of all the determinations including remelts.

melted again as the temperature rose. The reason for this was that barium oxide forms low-melting mixtures when contaminated by small quantities of barium carbonate and hydroxide and it was impossible to prevent the barium oxide from forming some of these materials before it was actually placed in the melting receptacle. By gradually increasing the temperature of the boat after the first melting occurred, the carbonate and hydroxide were easily decomposed and the carbon dioxide and water formed were pumped out of the system. As soon as this occurred the sample became solid again. This first melting made it difficult to obtain any data on particles of the most desirable size. Fifteen melts were taken and, as shown in Table I, the results obtained were in fairly good agreement with one another. A marked wetting of the tungsten by the barium oxide did occur, so that it was difficult to remove much barium oxide from the tungsten boats after melts. However, enough was obtained for several determinations with such previously melted material. In these experiments no great change in the melting point was observed. Tests were also made on samples of Kahlbaum's C. P. anhydrous barium oxide. The low-melting mixture mentioned above was also met here. The melting points obtained for these samples were essentially those obtained for barium oxide prepared by the decomposition of the carbonate. The results obtained for all of the work done on this oxide are given in Table I. The average temperature determined for the melting point of barium oxide was 2196°K.

Strontium Oxide.—Melting-point determinations were made on 15 different samples of this oxide. In the first of these experiments, Kahlbaum's C. P. strontium oxide was used. It behaved very similarly to calcium oxide while being tested. No low-melting mixture of oxide with small amounts of hydroxide and carbonate was encountered, and samples remelted several times showed no significant change in melting point. Samples of oxide prepared by decomposing pure strontium carbonate were also tested and the melting points obtained were essentially the same as those for Kahlbaum's oxide. A wetting of the tungsten boat by the strontium oxide occurred which, although somewhat more pronounced than that of the calcium oxide, was far less noticeable than that of the barium oxide. The experimental results are given in Table I. The average temperature determined for the melting point of strontium oxide was 2703°K.

Calibrations and Calculations

Calibration of Optical Pyrometer.—A disappearing filament type of optical pyrometer was used. As the temperatures to be measured were far above the working limits of the pyrometer lamp, absorption glasses were interposed between the lamp and the hot body.

From the data shown in Table I, it is seen that the different observations give temperatures that fall into definite groups. Thus in the case of strontium oxide, five of the observed temperatures were 2417°K., nine were 2423°K., and four were 2430°K., while there were no observed temperatures between these groups. These sudden jumps of six or seven degrees were due to the calibration of the pyrometer lamp.

The lamp was calibrated by relating the brightness of the filament to the heating current in milliamperes. The sensitivity of the lamp was such that a difference of 1 mil. was equivalent to about 5° temperature. Furthermore, the precision of the optical pyrometer method was such that a difference of about 5° in temperature could not be determined with certainty.

The lamp was originally calibrated at the Bureau of Standards, to give the true black-body temperature. This calibration was checked frequently, during the course of this work, against a standard lamp supplied by the Nela Research Laboratories.

Calculation of True Temperature.—Since the optical pyrometer was calibrated for a perfect black body under ideal light transmission conditions, the observed temperatures of the tungsten boat were not the true ones. However, the true temperature may be calculated from the observed or apparent one by the use of Wien's equation, if modified slightly to correct for the absorption and reflection of light by the glass of the containing vessel. The modified equation used is $(1/T)-(1/S_\lambda) = (\lambda/C_2)(ln\ e_\lambda + ln\ A)$. T is the true temperature and S_λ the observed pyrometer temperature in degrees Kelvin; λ is the wave length for which the pyrometer was calibrated, and in this case was 0.65μ; e_λ is the spectral emissivity of tungsten for the wave length λ at the temperature T. Since T is approximately known from the value S_λ, an approximate value of T is used in finding e_λ. The error made by doing this is negligible. The values of e_λ used in these experiments are given in Table I. These values were obtained from data appearing in a publication by Forsythe and Worthing.[9] For determining the constant A, a Marten's polarization photometer was used. The mean value found for this transmission coefficient A was 0.92. The constant C_2 was taken as 14,330, being the value adopted for the forthcoming International Critical Tables.

Discussion

Accuracy of Data.—The agreement between the melting temperatures obtained when different samples of the same oxides were tested shows that a high degree of precision may be obtained by this method. The value 2843°K. was obtained as the melting point of calcium oxide in 12 out of 21 of these determinations, and the average of the 21 is only 6° higher, as shown in Table I. In the case of the barium oxide, 14 of the 19 determinations gave 2193°K. as the melting point. The range of values was only 17°; the average temperature was 2196°K. The values obtained for strontium oxide are about equally well distributed on both sides of the average, 2703°K. That the results of this investigation were not only determined with great precision but also with considerable accuracy is indicated by the fact that the melting point obtained for calcium oxide agrees with the values of Kanolt and Ruff and Schmidt within 6°. At these high temperatures such a variation is negligible.

Effect of Wetting.—It was indeed unfortunate in these experiments that calcium oxide wet the tungsten boat to a less degree than did either barium or strontium oxide. The effect on the melting point of this wetting in the case of calcium oxide was presumably insignificant. If such was not the case, then it does not seem probable that results would have been obtained which were concordant with those obtained by Kanolt with an entirely different method. What effect wettings, such as were encountered in the cases of strontium and barium oxides, had on the melting point is questionable. The probability, however, of the readings being

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[9] Forsythe and Worthing, "The Properties of Tungsten and the Characteristics of Tungsten Lamps," *Astrophys. J.*, **61**, 146 (1925).

either appreciably high or low seems remote. Had remelted samples given quite different results from those obtained during the first melts, then these data would have been worthless. It is recognized that constancy of the melting point on remelted samples does not necessarily prove that impurities were not taken up which materially affected the results. However, it does seem reasonable to believe that if an impurity were taken up during the first melt, which materially affected the melting point of the sample, then during subsequent melts on the same sample, more of this impurity should have been taken up and some detectable variation in the melting point should have been noted.

Graphite Cylinder Method.[10]—Methods other than that just described were tried, in an attempt to get a check on the results obtained by the first method. Melts conducted in graphite containers gave low results. The alkaline earth oxides in contact with graphite rapidly form carbides when heated at high temperatures. The apparatus used in this method consisted of a graphite cylinder approximately 6 mm. in diameter and 50 mm. long. A hole of 3mm. diameter was drilled coaxially in the cylinder for practically its entire length. This was then tapped by two radial holes of the same size near the ends of the cylinder. The coaxial hole was then packed with the oxide, and the cylinder was placed vertically between two electrodes. A bell jar over the whole apparatus enabled a vacuum to be maintained. An optical pyrometer was used for measuring the temperature. The upper radial hole was used as gas vent, and the pyrometer was sighted on the lower one. The temperature at which the oxide first ran into this hole was taken as the melting point. Here no temperature correction was made, since approximately black-body conditions existed.

Conductivity Method.—A method that seemed at the start to give promise of success was first to press the oxide under test into rod form, and then to apply a potential of several hundred volts to the ends. At the same time the whole rod was heated in an oxyhydrogen flame in order to increase its conductivity. As soon as the current began to pass through the rod the external heating was suspended. Several strontium and calcium rods were melted. Not knowing, however, the emissivity of these oxides the actual data obtained showed only that the melting point of strontium oxide was less than that of lime.

Kanolt's Method.—A brief description of one of the methods used by Kanolt might be of interest. A tube made of lime was inserted into a furnace. It was supported by the upper end which was at a low temperature. The lower end was extended into the hot part of the furnace. He sighted a pyrometer down the tube and plotted a heating curve. Here, there was no chance of contamination by tungsten.

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[10] In some cases carbon cylinders also were used.

Summary

A new method of determining the melting points of certain oxides is described. The melting point of calcium oxide by this method was determined to be 2849°K., which is in good agreement with the generally accepted value 2843°K. determined in a different way by Kanolt. Similarly, the melting points of barium oxide and strontium oxide were found to be 2196°K. and 2703°K., respectively.

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NOTE

The Catalytic Decomposition of Hydrogen Peroxide in an Acid Chlorine-Chloride Solution.—Since the publication of our paper on the catalytic decomposition of hydrogen peroxide in an acid chlorine-chloride solution,[1] Mr. E. A. Guggenheim of Cambridge University has directed our attention to the fact that our derivation of Equation 33 (by means of which we computed the time required for the chlorine concentration to reach some definite fraction of its steady-state value) involves an error in logic. We obtained Equation 33 by combining Equation 31, which is quite correct, with Equation 32; but Equation 32 is incorrect, since it was obtained by integrating, between the limits $t = 0$ and $t = t$, the steady-state rate equation (No. 3) which does not fit the initial rate within 100%. However, a relation between the time and the ratio of the chlorine concentration to its steady-state value can be readily obtained in the following manner.

Since the concentrations of the chloride and hydrogen ions are assumed to be constant during any one experiment,[2] we may combine Equations 18, 19, 21, 22 and 26 with the steady-state relation $K_1/K_2 = y_s[H^+]^2[\mathrm{Cl}^-]^2$, and obtain the following equation.

$$\mathrm{d}y/\mathrm{d}t = K_1[\mathrm{H_2O_2}]\,[\mathrm{H}^+]\,[\mathrm{Cl}^-]\,(1 - y/y_s) \qquad \mathrm{A}$$

By means of Equation 31, $[\mathrm{H_2O_2}]$ may be expressed as a function of y,

$$[\mathrm{H_2O_2}] = [\mathrm{H_2O_2}]_0 - 2\,y_s\,ln(y_s/(y_s - y)) + y \qquad \mathrm{B}$$

where the last term, y (or ay_s), is negligibly small in comparison with the rest of the expression. Substituting in Equation A we obtain the following relation.

$$\frac{\mathrm{d}y}{\mathrm{d}t} = K_1\,[\mathrm{H_2O_2}]_0\,[\mathrm{H}^+]\,[\mathrm{Cl}^-]\,\frac{y_s - y}{y_s}\left(1 - \frac{2\,y_s}{[\mathrm{H_2O_2}]_0}\,ln\,\frac{y_s}{y_s - y}\right) \qquad \mathrm{C}$$

By integration between $y = 0$ and $y = ay_s$, and replacing $2\,K_1$ by K, we find,

$$t = -\,\frac{1}{K\,[\mathrm{H}^+]\,[\mathrm{Cl}^-]}\,ln\left(1 - \frac{2\,y_s}{[\mathrm{H_2O_2}]_0}\,ln\left(\frac{1}{1 - a}\right)\right) \qquad \mathrm{D}$$

Using this equation we may repeat the computations given on p. 2081

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[1] Livingston and Bray, This Journal, 47, 2069 (1925).

[2] See Ref. 1, p. 2080, lines 6–10.