explainable on the assumption of hydrolysis of the acetophenetide at this temperature with formation of free amine which latter acquires a blue coloration very quickly in the presence of air.

The solubilities of the liquid hydrate below the melting point of the solid under water, that is in the unstable region, were determined by first agitating the sealed tubes in a water-bath heated above the saturation temperature of the solid, until the last faint traces of crystals had disappeared, and then cooling. The procedure was then that of Rothmund.[1] Obviously for the 0.301 molecular per cent. concentration, it was only necessary to allow the tube to cool after determining the upper equilibrium point, since the latter was in the stable region. No supersaturation of the liquid hydrate in water was observed.

In concentrations greater than 0.301 molecular per cent., the requisite supercooling of the solution with respect to solid could not be obtained, the solid hydrate forming before all the liquid phase had dissolved. Nevertheless, enough points were determined on the solubility curve of the liquid hydrate in the unstable region to prove clearly that the liquid hydrate possessed a minimum of solubility in water and that this point lay in the unstable region.

Repeated attempts to discover a similar behavior of water dissolved in the fused hydrate were without result, due to inability to obtain sufficient supercooling with respect to the solid hydrate.

Summary.

The solubilities in water of the monohydrate of 3,5-dimethoxy-acetophenetide have been determined from 21.8° to 173.6°. The fused hydrate has been shown to possess a minimum of solubility in the region unstable with respect to liquid hydrate.

NEW YORK, N. Y.

THE STANDARDIZATION OF THE SULFUR BOILING POINT.[2]

BY E. F. MUELLER AND H. A. BURGESS.

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CONTENTS.—

I. Introduction.

The sulfur boiling point occupies a position of unusual importance among the thermometric fixed points on account of the care and accuracy with which its temperature has been determined, the precision with which

[1] *Loc. cit.*

[2] Publication of this paper has been authorized by the Director of the Bureau of Standards.

this temperature may be reproduced, but most of all on account of the very general practice of using it to determine one of the fundamental calibration constants of the platinum resistance thermometer, which serves as the most precise and convenient means now available for defining the temperature scale in the range —50° to +500°. The best measurements available are insufficient to show that the scale so defined differs from the thermodynamic scale in any part of this range.

The results of the best determinations of the temperature of the sulfur boiling point, on the thermodynamic scale, are summarized in Table I, which, with the exception of the last entry, is abbreviated from that given by Day and Sosman.[1]

TABLE I.

Determinations of the Temperature of the Sulfur Boiling Point.

Date.	Author.	Temperature thermodynamic scale. ° C.
1890	Callendar and Griffiths	444.91
1902	Chappuis and Harker	444.80
1908	Eumorfopoulous	444.93
1911	Holborn and Henning	444.51
1912	Day and Sosman	444.55
1914	Eumorfopoulous[2]	444.61

From the data of Table I it appears that any value which may be selected as representing the temperature of the sulfur boiling point may be in error by 0.1° or even 0.2°, and that fixing this point to a few hundredths of a degree, which is the precision attainable with a resistance thermometer, is at present a matter of definition. On the grounds that greater weight should be given to the newer determinations, but that the value is not known better than 0.1°, there is a choice as to whether 444.5° or 444.6° shall be selected. As none of the values is as low as 444.5° and all the older values are decidedly above this, the Bureau has adopted the value 444.6°. For the purpose of defining the scale of the platinum resistance thermometer, the temperature of the sulfur boiling point under standard atmospheric pressure is taken *by definition* as 444.60°.

Having decided upon the value to be used for the temperature of the sulfur boiling point, it is necessary to define the experimental conditions so as to make the temperature reproducible with the highest attainable precision in order that the temperature scale defined by the platinum resistance thermometer may also be as definite and reproducible as possible.

The effect of the experimental conditions, particularly as regards shielding of the thermometer, had been investigated by Callendar and Griffiths[3]

[1] *Am. J. Sci*, **33**, 530 (1912); *J. Wash. Acad. Sci.*, **2**, 174 (1912); *Ann. Physik*, **38**, 865 (1912).

[2] *Proc. Roy. Soc.* (*London*), **90A**, 189 (1914).

[3] *Phil. Trans.*, **182A**, 143 (1891).

and by Waidner and G. K. Burgess[1] and by others. More recently Meissner[2] reported further experiments which showed that the temperature assumed by a resistance thermometer in the sulfur vapor depended upon the reflecting power of the interior of the shield. His work raised some doubt as to the adequacy of the older work, but was incomplete in some respects; for example, it did not indicate to what extent the effectiveness of a given shield depended upon the nature of the material used for the protecting tube of the thermometer. Waidner and Burgess had also investigated the temperatures attained in various types of boiling-point apparatus. Apparently there has been no investigation of the effect of impurities in the sulfur upon the observed boiling point. The variation of temperature with pressure has been experimentally investigated by Holborn and Henning,[3] and by Harker and Sexton.[4]

As a result of these investigations the method of using the sulfur boiling point has, to a certain extent, become standardized. It has become the common practice to use a boiling tube of glass or like material about 5 cm. in diameter. Also it is generally recognized that the source and manner of heating should be so controlled as not to superheat the vapor, and that the thermometer must be suitably protected from the effect of loss of heat by radiation or otherwise, as without such protection the observed value may be a degree or more in error.

It is the purpose of this paper to present further evidence on the effect of these experimental conditions with the object of making this evidence sufficiently complete to serve as a basis for standard specifications for the use of the sulfur boiling point as a calibration temperature. The work was therefore planned so as to supplement and complete, in so far as possible, the work of the previous investigators.

II. Apparatus Used.

The greater part of the work was done with a gas-heated apparatus shown in Fig. 1. This is a development of the gas-heated apparatus which has been used regularly at the Bureau of Standards for some years.[5] The improvements are mainly in certain details which give greater ease and convenience of manipulation. The new apparatus was made to accommodate two lengths of boiling tubes, about 45 cm. and 70 cm., respectively, both of which were used, and the insulating jacket was made in two sections to suit the two lengths. The source of heat was a Méker blast burner, the flame of which played against a heavy ribbed iron casting containing a well about 7 cm. deep, in which the lower end of the

[1] Bur. of Standards, *Bull.* 6, 189 (1910); Bur. Standards, *Sci. Paper* 124.

[2] *Ann. Physik*, IV, 39, 1230 (1912).

[3] *Ibid.*, IV, 26, 859 (1908); 35, 772 (1911).

[4] *Report Brit. Assoc.*, 1908, p. 621.

[5] Waidner and Burgess, *Loc. cit.*, p. 187.

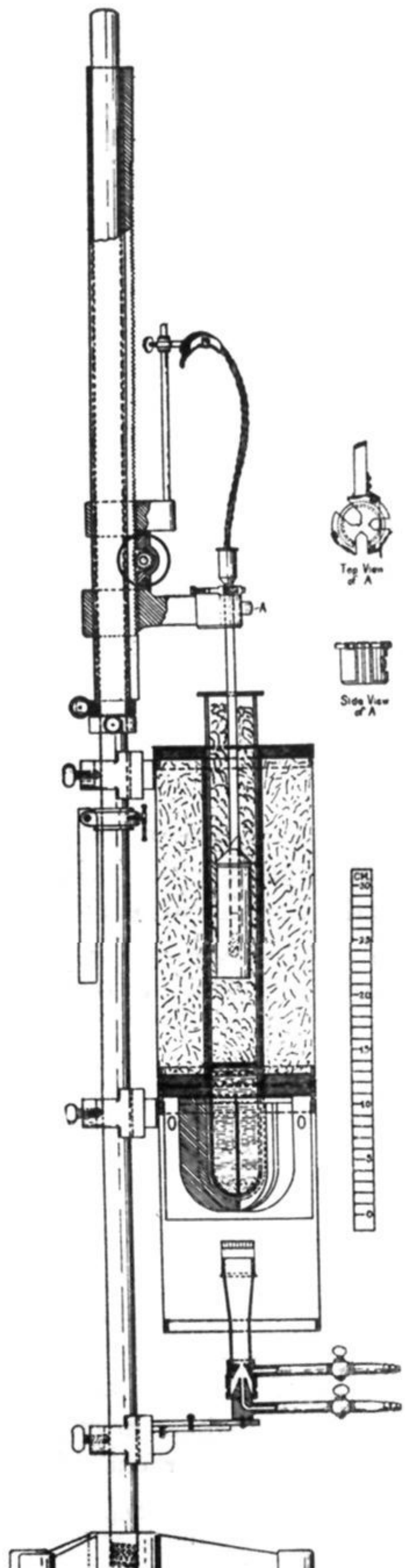


Fig. 1.—Gas heated sulfur boiling apparatus.

boiling tube rested. The liquid sulfur surface was kept about 5 cm. above the top of this casting to prevent superheating of the vapor. The thermometer was held in a specially designed clamp which could be opened or closed quickly by one motion and which, when once set in position, held the thermometer always in alignment and concentric with the boiling tube. This clamp was carried on a rack and pinion carriage which moved up and down, on the main vertical supporting rod of the apparatus, which was equipped for a scale for reading directly the position of the thermometer coil inside the boiling tube. The heat insulation was very efficient and the sulfur could be brought to boiling sufficiently for an observation in less than an hour after starting.

Both glass and fused quartz tubes were used, the latter provided with a narrow, fused in window of transparent quartz near the top, through which the line of condensation could be observed. Ample opening was left in the cover of the boiling tube for an equalization of pressure inside and outside the tube.

The apparatus is so arranged that the ribbed casting and the burner can be removed and an electric heater substituted. This heater consists of a porcelain tube, 15 cm. long, having an inside diameter 5 to 10 mm. larger than that of the boiling tubes used. The heating coil is of nichrome tape wound on the porcelain. The top of this porcelain tube occupies the same position as the top of the ribbed casting, and the heating coil covers the upper 8 cm. of it. The boiling tube extends into this tube, about 7 cm. resting on a cushion of soft asbestos.

A heater of this type had been improvised for some special experiments and proved so satisfactory that the heater described above was built and has superseded the gas heater.

The resistance thermometers used were made in the usual form with cylindrical coils and were enclosed in glass or porcelain tubes. Some of the thermometers were provided with interchangeable glass and porcelain tubes. The coils were of the strain-free type[1] and the leads were so fastened to the supporting mica strips that any strain on the leads could not be communicated to the coil. The connections were of the potential terminal type. Resistances were measured with a mercury contact Wheatstone bridge together with a commutator according to the method recently described.[2]

The coils of thermometers C_{26}, C_{27} and C_{28} are about 4.5 cm. long and the protecting tubes are 5 mm. internal, 7 mm. external diameter, which is about the same as the external diameter of the ordinary chemical thermometers. The coil of C_{22} is about 8 cm. long and the protecting tube is 8 mm. internal, 10 mm. external diameter.

A Fuess siphon type barometer, which could be read to an accuracy of 0.02 to 0.04 mm. was used for the measurements of atmospheric pressure. All pressures were expressed in the equivalent millimeters of mercury at 0°, and under standard gravity ($g = 980.665$).

III. Description of Experiments.

a. **Comparison of Radiation Shields.**—The types of shields used are illustrated in Fig. 2. The openings at the tops of the shields were made

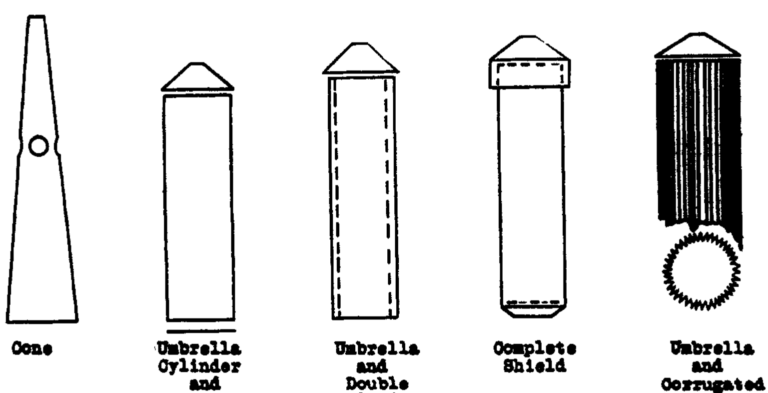


Fig. 2.—Radiation shields.

to fit the thermometer tubes closely. All the shields were made so that any openings in them were at least 2 cm. above or below the coils of the thermometers.

[1] Waidner and Burgess, *Loc. cit.*, p. 115.

[2] Mueller, Bur. Standards, *Bull.* **13**, 547 (1916); Bur. Standards, *Sci. Paper* **288**.

For the comparative tests, the resistance and corresponding barometric pressure were observed for 4 different depths of immersion of the thermometer with its attached shields, these positions being such that the bottom of the shield was 6, 8, 10 and 12 cm., respectively, above the surface of the liquid sulfur. Time was allowed for the establishment of equilibrium before each reading. In most of the experiments the variations of temperature observed, accompanying the above displacements, were within the limits of observational error (less than 0.02°) and this constancy was a valuable indication of suitable experimental conditions. Where such constancy was not observed the fact is noted in the tables. In all cases the result given in the tables is the one obtained from the readings at the 8 cm. height.

The temperature of the vapor was deduced from the barometric pressure by use of the formula

$$t = 444.60^\circ + 0.0910(p = 760) - 0.000049(p - 760)^2$$

which is based on data given later in this paper.

The comparison of the temperatures as observed with the resistance thermometers is made most conveniently by computing for each observation the platinum temperature, designated Pt_{760}, corresponding to standard barometric pressure.

By differentiating the Callendar formula

$$t - pt = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \quad \text{where } pt = \left(\frac{R_T - R_0}{R_{100} - R_0}\right) 100$$

a relation

$$dpt = \left(1 + \frac{\delta}{100} - \frac{2\delta t}{100^2}\right) dt$$

is found, which for values of $\delta = 1.495$ and $t = 444^\circ$ becomes

$$\Delta\, pt = 0.882\, \Delta t.$$

This equation is applicable for the entire range of barometric pressures and for all the values of δ occurring in this series of experiments.

The comparative data for various shields, all obtained in the gas heated boiling apparatus, are assembled in Table II, being classified according to kind of shield used. The table shows the number of the thermometer, the material of the thermometer protecting tube, the type of shield used, the platinum temperature corresponding to standard barometric pressure as calculated from each observation, and the amount by which this is *lower* than the average platinum temperature found with all the shields which were adequate.

Fortunately, the facts brought out in Table II can be very briefly summarized. It will be noted that all the iron shields, either with or without the lower disc, gave practically the same value of Pt_{760}, for any one thermometer, and the mean of all the values obtained with these shields may be considered the standard value. Since it is evident that no shield can cause the thermometer to assume a temperature higher than that of the vapor, it follows that low values of Pt_{760} indicate inadequate shielding. All of the data substantiate Meissner's conclusion that a shield, the inner surface of which is a good reflector, will be ineffective. This is now shown to be true whether the thermometer is enclosed in glass or in porcelain. Thus the iron shields, the Callendar-Griffiths shield, graphite cylinder, asbestos cone, an aluminum shield, blackened inside, are all effective. Even an aluminum cylinder, with the walls sharply corrugated, forming a series of wedges, which is therefore a good radiator, was as effective as the other shields.

A complete aluminum shield was nearly realized in a cylindrical shield with overhanging umbrella and the lower edge of the cylinder extending below the lower disc and curving inwards, so that all direct radiation from the platinum coil in any direction met the shield, while a free circulation of vapor was possible. With this shield the thermometer read 0.02° or 0.03° lower than when enclosed in the adeqaute shields previously mentioned.

The data for the other aluminum shields, with bright inside surfaces, show that the temperature attained by a thermometer enclosed in such a shield depends upon the form of the shield, primarily upon the extent to which the shield forms a complete enclosure, upon the extent to which the interior of the shield has become dull or blackened, and also upon the material (transparency) of the protecting tube of the thermometer. The readings obtained range from 0.2° low, obtained with a simple cone on a glass enclosed thermometer to 0.02° low, obtained with a nearly closed shield on a porcelain enclosed thermometer. The extreme lowerings found were 0.2° for a glass enclosed thermometer and 0.1° for a porcelain enclosed thermometer.

Inadequate shielding is also usually accompanied by considerable variations in temperature, sometimes amounting to 0.1°, when the thermometer is displaced vertically, but the absence of such variation is not necessarily proof of adequate shielding. It may also be remarked in passing that the absence of such variations does not prove that there is no superheating of the vapor, as in one instance constant temperatures were observed with a displacement of 4 cm. where, owing to insufficient depth of liquid sulfur in the tube, the vapor was superheated about 0.5°.

These results are in the main in agreement with those of Meissner, in so far as they cover the same field. They differ from his in regard to the effectiveness of nearly closed aluminum shields, which, according to our results, are more effective than Meissner found them to be. How-

TABLE II.—COMPARISON OF SHIELDS IN GAS HEATED APPARATUS.

Obs. No.	Therm. No.	Tube enclosing thermometer.	Description of shield.	Pt_{760}. Degrees.	Lowering of Pt_{760}. Degrees.	Remarks.
			A. Iron Shields.			
1	C_{26}	Porcelain	Cone	421.65	0.00	Average for C_{26}, 421.65
2	C_{27}	Porcelain	Umbrella and Cone	421.72	0.00	
3	C_{27}	Glass	Umbrella and Cone	0.73	—0.01	
10	C_{27}	Glass	Umbrella and Cyl.	0.72	0.00	
15	C_{27}	Glass	Umbrella and Small Cyl. 23 mm. diam.	0.71	+0.01	
16	C_{27}	Glass	Umbrella, Cyl. and Disc.	0.73	—0.01	
17	C_{27}	Glass	Umbrella	0.69	+0.03	Reading unsteady
18	C_{27}	Glass	Umbrella and Double Cyl.	0.74	—0.02	Average for C_{27}, 421.72
19	C_{28}	Glass	Cone	421.67	0.00	
21	C_{28}	Glass	Umbrella and Double Cyl.	0.68	—0.01	
23	C_{28}	Glass	Umbrella and Cyl.	0.67	0.00	
24	C_{28}	Glass	Umbrella and Small Cyl. 23 mm. Diam.	0.65	+0.02	
25	C_{28}	Glass	Umbrella and Small Cyl. 23 mm. Diam.	0.66	+0.01	
26	C_{28}	Glass	Umbrella and Cyl. 30 mm. Diam.	0.66	+0.01	
27	C_{28}	Glass	Umbrella and Cyl. 33 mm. Diam.	0.68	—0.01	
28	C_{28}	Glass	Umbrella and Cyl. 32 mm. Diam.	0.68	—0.01	Average for C_{28}, 421.67
			B. Modified Aluminum Shields.			
30	C_{27}	Glass	Umbrella and Cyl. blackened inside	0.72	0.00	
35	C_{27}	Glass	Umbrella and corrugated cyl.	0.71	+0.01	
36	C_{27}	Glass	Umbrella corrugated cyl. and disc.	0.72	0.00	

C. Miscellaneous Shields.

37	C_{27}	Glass	Graphite umbrella and cyl.	421.73	−0.01	
38	C_{27}	Glass	Asbestos cone	0.71	+0.01	
40	C_{27}	Glass	Callendar-Griffiths	0.73	−0.01	

D. Bright Aluminum Shields. Inadequate Shielding.

41	C_{26}	Porcelain	Cone	421.58	+0.07	
42	C_{27}	Porcelain	Umbrella, cone and disc.	0.70	+0.02	
43	C_{27}	Porcelain	Cone and disc.	0.68	+0.04	
44	C_{27}	Glass	Umbrella and cyl.	0.51	+0.21	
45	C_{27}	Porcelain	Umbrella, cyl. and disc.	0.66	+0.06	Old dull shield
46	C_{27}	Porcelain	Umbrella, cyl. and disc.	0.60	+0.12	New bright shield
47	C_{27}	Glass	Umbrella cyl.	0.62	+0.10	Unsteady
48	C_{27}	Glass	Umbrella cyl.	0.60	+0.12	
49	C_{27}	Glass	Complete shield	0.70	+0.02	
50	C_{27}	Glass	Complete shield	0.69	+0.03	
51	C_{28}	Glass	Cone	0.48	+0.19	
52	C_{28}	Glass	Umbrella and cone	0.49	+0.18	
53	C_{28}	Glass	Umbrella, cone and disc.	0.60	+0.07	

ever, there is agreement on the essential point that no bright aluminum shield is completely effective.

Tight Fitting Umbrella Not Necessary.—In most of the shields used, the hole in the center of the umbrella was made to fit the thermometer tube rather closely. Some observers have recommended using asbestos string tied around the thermometer tube just above the umbrella. This was also tried and found to be unnecessary, and, on account of its inconvenience, is regarded as undesirable. Even entirely omitting the umbrella, and using only a cylindrical iron shield open at both ends, around the coil, produced a lowering of only about 0.05°.

Temperature of Shield.—Apart from the effect of the shield upon the temperature assumed by the thermometer, it is of some interest to determine the temperature of the shield itself. If the thermometer be enclosed in a long, close-fitting, closed-end metal tube, the thermometer coil should assume the temperature of the tube, and the tube, although differing in form, perhaps assumes a temperature not differing much from the temperature assumed by a shield. In this way an iron tube with umbrella above was found to have a temperature about 0.15° lower than that assumed by an adequately shielded thermometer, while an aluminum tube assumed a temperature only about 0.01° lower. Without the umbrella the iron tube had a temperature about 0.3° lower and the aluminum shield a temperature about 0.04° lower than that assumed by a shielded thermometer.

The higher temperature assumed by the externally polished aluminum shield might have been predicted from theoretical considerations, since the aluminum is a poor radiator. It would appear that the best single shield would have a polished exterior and blackened interior, but we have not recommended the adoption of such a shield to the exclusion of other forms because of the difficulty of preparing such shields, and because observation of the temperature of the thermometer enclosed in such a shield shows that the advantage is purely a theoretical one.

Preferred Type of Shield.—From the result of the experimental work described we have come to the conclusion that in general the best type of shield is a simple sheet iron cylinder from 1.5 to 2.5 cm. larger in diameter than the thermometer tube and about 4 cm. or more longer than the coil, open below and with an umbrella above. This umbrella should fit the thermometer tube closely and extend beyond the edge of the cylinder, leaving the space 5 mm. to 1 cm. high between umbrella and cylinder for circulation of the vapor. For the material of the shield sheet iron is preferred in general. The main objection to the iron shield seems to be that the sulfur attacks the iron and forms considerable scale, as a result of which the iron is consumed and the bath discolored, although without affecting the temperature of the boiling point. Practically all the loose scale is formed when the shield is withdrawn from the bath, however, when the sulfur takes fire spontaneously, so that only a small amount of scale need be left in the boiling tube if care is taken. The life of the iron shield is longer than might be expected, one in particular that had been used a dozen times did not appear appreciably thinner than when first made. This objection to the iron shield is not a serious matter in view of the high and consistent readings obtained with it.

It is possible that the slightly higher temperature (0.01° or at most 0.02°) obtained with the double iron shields may not be attributable entirely to experimental error, and that the use of a single shield will result in slightly low readings. The difference is so small, however, that it seems desirable to standardize the single shield for use in the sulfur boiling-point apparatus, in the interest of simplicity. It should be noted that in the electrically heated apparatus this difference was not found. (See Table III.)

In cases where the iron is objectionable, aluminum, blackened on the inside, may be substituted, and in case it is desirable to introduce nothing but aluminum into the bath, a corrugated aluminum shield is satisfactory, although it requires more time to make. Once made, it is perhaps the most satisfactory of any. Any of the three shields mentioned have been shown to satisfy sufficiently well the following criteria of effective shielding:

1. The reading must not change more than 0.02° upon moving the thermometer with the shield up and down in the vapor column for at least 6 cm., *e. g.*, from 6 to 12 cm. above the liquid surface.

2. The reading must be steady,—if fluctuations amounting to even 0.01° are present, a readjustment should be made.

3. The readings should be capable of being repeated from day to day to within 0.03°.

4. The use of the shield should lead to the same value of Pt_{760} for a given thermometer regardless of the thermometer protecting tube.

5. The use of the shield must not lead to different readings with age or repeated use.

6. Doubling the shield, *i. e.*, putting a shield within a similar one, should not change the indications of the thermometer.

7. The use of the shield should lead to as high a reading as would be obtained by using any other form of shield.

b. **Comparison of Types of Boiling Apparatus.**—To test for possible effects of differences in methods of heating, in dimensions and in the heat insulation around the tube, several types of boiling apparatus were constructed and experiments were made to determine the effects of various types of insulation around the boiling tube.

An electrically heated boiling apparatus was built along the lines of the one used by Meissner and described in his paper, the main difference being that the heating coil did not extend under the boiling tube but was wound on an outer porcelain tube, the coil extending upwards from a point about on a level with the bottom of the sulfur-containing tube for a distance of about 6 cm. The bottom of the porcelain tube which extended somewhat below the heating coil was closed with asbestos board. An auxiliary heating coil was wound on the upper part of the porcelain tube to hasten the boiling but was disconnected at least half an hour before observing. The porcelain tube was 30 cm. long, the inner diameter being about 4 mm. greater than the outer diameter of the boiling tube, and thus a small air space was left between the two similar to that shown in Meissner's drawing. This apparatus proved very effective in heating up quickly on about 400 watts, and readings taken on different days were about as consistent as those observed with the gas heated apparatus.

Nine observations were taken in this apparatus with two thermometers, C_{27} and C_{28}, the former having a glazed porcelain tube and the latter a glass tube. Comparing these observations, which are shown in Table III, with those made in the gas-heated apparatus, using adequate shields in both cases, C_{27} gives a value for electric heating 0.01° higher than for gas heating, and C_{28} gives a value for electric heating 0.03° higher than for gas heating. The readings were remarkably constant for displacements of the thermometers up and down for a distance of more than 10 cm., the usual variation not exceeding 0.01°. In this type of boiling apparatus there is a possibility that the vapor may be superheated owing to conduction up to the porcelain tube, or to convention of highly heated air in space between the porcelain tube and the boiling tube.

Through kindness of Messrs. Day and Sosman, the electrically heated apparatus was made available in which their direct determination of the sulfur boiling point by the gas thermometer was carried out. The boiling tube of this apparatus is 71 mm. internal diameter, while that of the specially constructed apparatus above described is 42 mm. A direct comparison of the two was made by interchanging thermometer C_{28} from one to the other, resulting in a value for the large tube about 0.03° lower than for the small tube. The temperature observed in the large tube was therefore the same as that observed in the gas-heated apparatus previously described.

A tube of small diameter (25 mm. internal) was also used as a boiling tube. It was heated with a gas burner and insulated with sheet asbestos. Measurements in this tube indicated superheating of the vapor and considerable differences of temperature at different heights in the tube.

Effect of Surroundings of Tube.—In order to determine to what extent the heat insulation and the character of the surface next to the boiling tube, whether this surface be a good or a poor reflector, might influence the reading of the thermometer, a 70 cm. boiling tube was used in a short

TABLE III.—OBSERVATIONS WITH ELECTRICALLY HEATED SULFUR BOILING APPARATUS.

Therm. No.	Tube enclosing thermometer.	Type of shield.	Pt_{760}.	Remarks.
		A. Meissner Type.		
C_{27}	Porcelain	Umbrella and Iron Cone	421.725	
C_{27}	Porcelain	Umbrella and Iron Cone	0.75	
C_{27}	Porcelain	Umbrella and Iron Cone	0.735	
C_{27}	Porcelain	Callendar-Griffiths	0.735	
C_{27}	Porcelain	Umbrella and Iron Cyl.	0.72	Average for C_{27}, 412.73[a]
C_{28}	Glass	Umbrella and Iron Cyl.	421.70	
C_{28}	Glass	Umbrella and Iron Cyl.	0.69	
C_{28}	Glass	Umbrella and Iron Cyl.	0.70	
C_{28}	Glass	Umbrella and Double Iron Cyl.	0.70	Average for C_{28}, 421.70[b]
		B. Day and Sosman Boiling Tube.		
C_{28}	Glass	Umbrella and Iron Cyl.	421.67	

[a] Average for gas heated apparatus is 421.72.
[b] Average for gas heated apparatus is 421.67.

jacket, leaving about 30 cm. of the tube extending out into the air. By using a very large flame, it was possible to raise the condensation line high enough to obtain a boiling-point observation in that portion of the tube surrounded only by the air. Boiling-point observations were made under this condition and with the tube surrounded with sheet iron, nickel foil, and thin sheet asbestos. The results are given in Table IV.

TABLE IV.

Effect of Surroundings of Boiling Tube upon Indications of Thermometer C_{27} with Porcelain Enclosing Tube, Shielded with Iron Umbrella and Cylinder.

Material surrounding boiling tube.	Pt_{760}.
Air	421.64
Sheet iron	0.68
Nickel foil	0.71
Thin asbestos	0.72
Thick insulation	0.72

From the two sets of experiments last described it appears that it would be well to set a lower limit, say 4 cm. to the diameter of the tube in the standard form of boiling apparatus. While it is necessary to provide some insulation for the tube, it is evident that a very small amount is sufficient and that the amount used will be dictated by considerations of efficiency.

c. **Purity of Sulfur.**—Small known quantities of arsenic and selenium were added to boiling pure sulfur and the boiling point observed in the usual way after each such addition. These materials were selected as being the most probable impurities occurring in ordinary sulfur which might be expected to affect the boiling point. The results are given in Table V.

TABLE V.

Effect of Added Impurities on the Boiling Point of Sulfur.

Condition of sulfur.	Pt_{760}.
Pure	421.73
With 0.05% arsenic added	0.73
With 0.1 % arsenic added	0.75
With 0.05% selenium added (plus the 0.1% arsenic)	0.81
With 0.1% selenium added (plus the 0.1% arsenic)	0.82

It is evident that selenium, even in small amounts, would be objectionable. All previous experiences indicate, however, that such impurities are not likely to be found in purified sulfur. This is further confirmed by the fact that the boiling point of a sample of crude sulfur from Louisiana was found to be not over 0.01° higher than that of the purified sulfur used regularly. The crude sulfur was part of a specimen exhibited in the local office of the Southern Railway Company, and was supplied through the courtesy of their local representative.

d. **The Relation between the Vapor Pressure of Sulfur and Temperature.**—The excellent agreement between the results obtained by Holborn and Henning and by Harker and Sexton might be taken to indicate that any repetition of their work would be superfluous. However, in the present investigation an extended comparison of shields was made during a considerable time interval and involving a range of barometric pressure of from 747 to 763 mm., and an equation was necessary which would represent the pressure-temperature relation of sulfur vapor to an accuracy of the order of 0.01°. An examination of Holborn and Henning's data indicated that the excellent agreement of the two sets of observations might have been to some extent, at least, fortuitous, and this, together with the fact that Harker and Sexton's data could not be obtained at all, made it appear desirable to redetermine the relation. The present work gave results in agreement with the older formulas, but a considerably higher degree or precision was obtained in the measurements.

The pressure control apparatus is shown diagrammatically in Fig. 3. The boiling tube was closed by a rubber stopper protected from the heat and from contact with the sulfur vapor by a disc of asbestos. Connection was made with 8 mm. internal diameter tubing through a trap of 2 liters' capacity, to the water manometer and to the pressure regulator. The manometer was made of 11 mm. internal diameter glass tubing and was equipped with mirror and millimeter scale for reading menisci. The pressure regulator was an ordinary 5 cubic-foot meter-prover with water seal. This proved admirable for pressure control since it took up any fluctuations of pressure. By means of levers and weights any desired pressure in the range from 700 to 800 mm. could easily be produced and maintained regardless of changes in temperature, etc. Simultaneous readings were made of the thermometer, manometer and barometer.

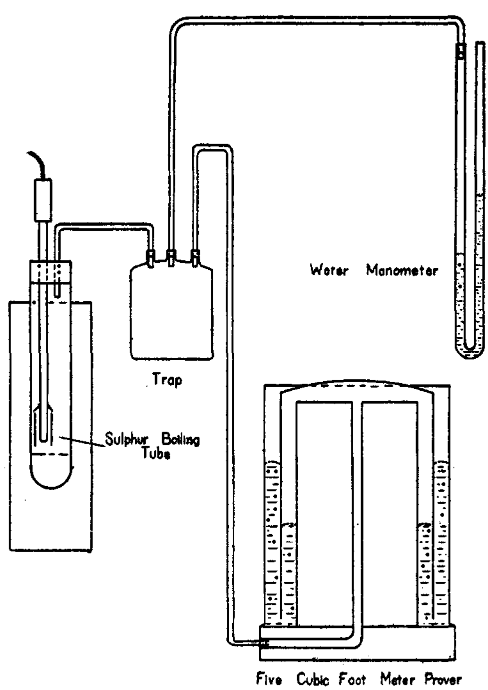
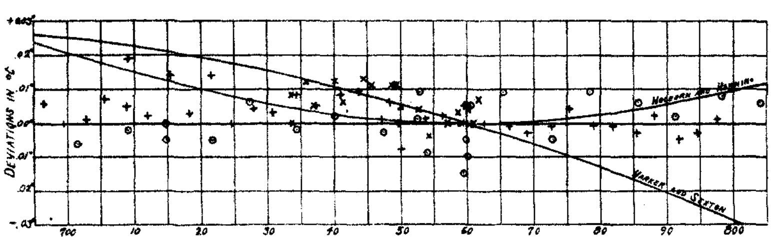


Fig. 3.—Apparatus for varying and measuring pressure of boiling sulfur.

In each series of observations, readings were first taken at one or two pressures very near to 760 mm., then the pressure was increased (or decreased) step by step, to the highest (or lowest) attainable with the apparatus, then changed step by step to obtain points intermediate between those previously observed, until the pressure of 760 mm. was again obtained. Further observations at pressures below (or above) 760 mm. were then made. In computing the pressures, account was taken of the density of the water in the manometer, the expansion of the manometer scale, and of the differences in level between the thermometer in the sulfur vapor, the water menisci and the barometer, in addition to the usual barometric corrections. From the considerable number of observations at pressures near 760 mm. a value of δ was computed, and in this way the curve was made to pass through the point $t = 444.60°$, $p = 760$. This method of computation might involve the use of a value of δ differing by one or two units in the third decimal place, from the best value of δ for that thermometer, but insured the agreement of observed and calculated values for normal pressure.



× Observations with thermometer C_{27}. May 26, 1916.
+ Observations with thermometer C_{27}. June 20, 1916.
○ Observations with thermometer C_{22}. June 23, 1916.

POSITIVE VALUES OF THE ORDINATES INDICATE HIGHER TEMPERATURES THAN THOSE CALCULATED FROM THE EQUATION

$t = 444.60 + 0.0910\,(p - 760) - 0.000049\,(p - 760)^2$. (Mueller and Burgess.)

OTHER EQUATIONS.

$t = t_{760} + 0.0910\,(p - 760) - 0.000043\,(p - 760)^2$. (Holborn and Henning.)

$t = t_{760} + 0.0904\,(p - 760) - 0.000052\,(p - 760)^2$. (Harker and Sexton.)

Fig. 4.—Observed minus calculated values of temperature plotted against pressure.

Three series of observations, and two thermometers were used. All of the observed points are reproduced in Fig. 4 in which the deviation of the observed temperature from that calculated by means of the equation

$$t = t_{760} + 0.0910\,(p - 760) - 0.000049\,(p - 760)^2$$

which was found to represent the observations, is plotted against the pressure. The deviations of Holborn and Henning's equation and of Harker and Sexton's equation from the above equation are also shown in Fig. 4.

IV. Summary.

The importance of the sulfur boiling point as defining a standard temperature, and the necessity of obtaining further evidence upon certain questions concerning the effect of experimental conditions upon the results obtained in its use, are considered.

The work of Meissner, which showed that the reflecting power of the inner surface of a radiation shield may have a considerable effect upon the temperature assumed by a resistance thermometer in the sulfur boiling-point apparatus, has been confirmed and extended. A number of types of shields were found to be satisfactory.

The influence of the type of boiling apparatus upon the observed temperature was found to be very small.

The effect of certain impurities in the sulfur upon the observed boiling point was investigated.

The change of vapor pressure with temperature, over the range of pressures from 700 to 800 mm., was redetermined.

Appendix.

Proposed Standardization of the Sulfur Boiling Point.—All experimental work published has been drawn upon in the preparation of these specifications. The specifications relate to apparatus and procedure suitable for the standardization primarily of resistance thermometers and thermocouples, and it was therefore considered permissible to limit the type of apparatus somewhat closely. The aim has been to impose conditions which are sufficient to insure that the thermometer shall assume a definite temperature, dependent only on the pressure, when placed in the apparatus, and the question as to whether these conditions are really necessary, has received only secondary consideration. Thus the question as to the temperature attained in tubes larger or smaller than those specified need not be considered. It may further be supposed that the thermometer or couple will be mounted in a protecting tube or sheath, and that the diameter of such a tube, or width of the sheath, will be less than 2 cm.

The specifications relate to the following matters: 1. Boiling Apparatus; 2. Purity of Sulfur; 3. Radiating Shield; 4. Procedure; 5. Computations.

1. Boiling Apparatus.—The boiling tube is of glass, fused silica or similar material, and has an internal diameter of not less than 4 nor more than 6 cm. The length must be such that the length of the vapor column, measured from the surface of the liquid sulfur to the level of the top of the insulating material surrounding the tube shall exceed the length of the thermometer coil by at least 20 cm.[1] Heating is by any suitable

[1] This length was arrived at as follows: The minimum distance from the liquid surface to the bottom of the shield, was taken as 6 cm., excess length of shield over length of thermometer coil, 6 cm.; distance available for displacing thermometer, 6 cm.; minimum distance from top of shield to level of top of insulation, 2 cm.

heater at the bottom of the tube, and the arrangement must be such that the heating element, and all conducting material in contact with it terminate at least 4 cm. below the level of the liquid sulfur. If a flame is allowed to impinge directly on the tube the heat insulation must extend at least 4 cm. below the level of the liquid sulfur. There should be a ring of insulating material above the heater, fitting the tube closely, to prevent superheating of the vapor by convection currents outside the tube. Above the heater the tube is surrounded with insulating material, not necessarily in contact with it, and of such character as to provide heat insulation equivalent to a thickness of not less than one cm. of asbestos. The length of this insulated part has already been specified. Any device used to close the top of the boiling tube must allow a free opening for equalization of pressure.

2. **Purity of Sulfur.**—The sulfur should contain not over 0.02% of impurities. It should be tested to determine whether selenium is present.

3. **Radiation Shield.**—The radiation shield consists of a cylinder open at both ends, and provided with a conical umbrella above. The cylindrical part is to be 1.5 to 2.5 cm. larger in diameter than the protecting tube of the thermometer, and at least one cm. smaller than the inside diameter of the boiling tube. The cylinder should extend 1.5 cm. or more beyond the coil at each end. The umbrella should fit the thermometer tube closely, should overhang the cylinder and be separated from the latter by a space 0.5 to 1.0 cm. high. The inner surface of the cylinder must be a poor reflector, such as sheet iron, blackened aluminum, asbestos, or a deeply corrugated surface.

4. **Procedure.**—The sulfur is brought to boiling[1] and the heating is so regulated that the condensation line is sharply defined and is one cm. or more above the level of the top of the insulating material. The thermometer, enclosed in its shield, is inserted into the vapor, taking care to have the thermometer coil properly located with respect to the shield, and the thermometer and shield centered in the boiling tube. After putting the thermometer into the vapor, time must be allowed for the line of condensation again to reach its proper level. Simultaneous readings of the temperature and barometric pressure are then made. In all cases care should be taken to prove that the temperature is not affected by displacing the thermometer 2 or 3 cm. up or down from its usual position.

[1] If the sulfur has been allowed to solidify in the bottom of the tube, it must be melted from the top downwards, to avoid breaking the tube. A better procedure is that recommended by Rothe (*Z. Instrumentenk.*, **23**, 366 (1903)), *viz.*, on completing work with the apparatus, it is turned so that the tube makes an angle of 30° or less with the horizontal, so that the sulfur on solidifying extends along the sides of the tube, in which position it may be melted down with less danger of breaking the tube. Even when the procedure recommended is followed, breakage of tubes may be reduced by carefully melting the sulfur from the top downwards over a bunsen burner, before applying heat to it in the apparatus.

5. Computations.—Temperatures are calculated from the pressure by use of the formula

$$t = 444.60° + 0.0910\ (p - 760) - 0.000049\ (p - 760)^2.$$

If necessary, account should be taken of any difference in pressure between the levels at which the thermometer bulb and the open end of the barometer, respectively, are located. Pressures are to be expressed in the equivalent millimeters of mercury at 0° and under standard gravity (g = 980.665).

WASHINGTON, D. C

NOTE.

Jellies by Slow Neutralization.—In a research with R. E. Rindfusz[1] we found that jellies of excellent texture and clearness could be obtained by peptizing ferric arsenate with ferric chloride and dialyzing the resulting colloid. Although at first some ferric chloride was found in the dialysates later only hydrochloric acid passed through the membrane. It was evident that gel formation depended on the slow removal of the acid derived from the hydrolysis of ferric chloride. In fact, when the ferric arsenate precipitate was peptized by barely enough ferric chloride rather than by a decided excess the gel formed more quickly and was not as clear nor of so good a texture. The small amount of hydrochloric acid developed was dialyzed out too rapidly to insure the best gel structure. Without question the time element is of prime importance.

We believed that dialysis disturbed the equilibrium indicated below.

$$Fe_2(HAsO_4)_3 + 6HCl \rightleftharpoons 2FeCl_3 + 3H_3AsO_4.$$

The ferric hydroxide resulting from hydrolysis of the ferric chloride is adsorbed in the gel structure by the ferric arsenate. Addition of any base would, of course, neutralize the hydrochloric acid and thus remove the hydrogen ion as effectually as is done by dialysis. But if this is attempted, a lumpy precipitate results. It occurred to us that if the hydrochloric acid could be neutralized slowly enough a gel of good texture must result. To test this we filled a bottle to the top with colloidal ferric arsenate (peptized by ferric chloride) and tied a membrane of goldbeater's skin over the mouth of the bottle, taking care that the membrane was in contact with the liquid.

On top of the membrane we attached a glass tube by a wide rubber band. In this upper vessel we poured about 2 cc. of N ammonium hydroxide. After 6 or 8 days a beautiful, clear gel resulted, red by transmitted light and smoky gray by reflected light. The ammonium hydroxide slowly dialyzed into the colloid neutralizing the hydrochloric acid at a rate permitting the formation and hydration of the ferric arsenate into

[1] THIS JOURNAL, 38, 1970 (1916).