# ON THE CONSTANCY OF THE SULPHUR BOILING POINT

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In view of the general use and convenience of the sulphur boiling point as a temperature for the standardization of thermometric apparatus, it is highly desirable to demonstrate conclusively by experiment that we are really dealing with a strictly reproducible and satisfactorily constant temperature throughout the column of vapor in the standard form of sulphur boiling apparatus, which is generally used.

We have recently shown [1] that in the ordinary form of Callendar and Griffiths apparatus, in which the sulphur is boiled in a glass tube some 45 cm long by 4.5 cm diameter, heated from below either electrically or by a gas burner, and in which the thermometer coil, mounted within a porcelain tube glazed on the outside, is inclosed in a cylindrical or conical radiation shield of aluminum of some 15 cm in length; the temperature of the sulphur vapor, as measured with resistance thermometers having coils 4 to 5 cm long, is apparently constant to within 0°.03 C throughout some 27 cm of the 30 cm length of the column of sulphur vapor.

With thermocouples of platinum-rhodium and of platinum-iridium, however, discordant results were obtained, varying both with the couple and depth of immersion of the wires in the vapor and indicating an apparent point-to-point variation within the radiation shield of the order of 0°.5 C.

Since it might be maintained that the relatively long resistance thermometer is an integrating device giving an average temperature within the shield whose real temperature would be far from constant as shown by the thermocouples which presumably give

[1] This Bulletin **6**, pp. 149–230; 1910.

the temperature at a point, we have thought it worth while to endeavor to remove any existing doubts as to the constancy of the temperature of sulphur vapor in this apparatus by further experiments.

It should first be noted, perhaps, that the resistance thermometer, if it can be made small enough, is more suited than the thermocouple for the measurement of small differences in temperature at the sulphur point, as the indications of the former, read as a strictly potential instrument, may be freed from any thermoelectric phenomena occurring in the lead wires; whereas in the case of the latter, such effects are additive, and when they occur in the platinum or alloy leads can not be distinguished from the E. M. F. of the junction.

We have therefore used, for the exploration of the temperature in the sulphur apparatus, in addition to several thermocouples, a resistance thermometer of very short coil, less than 9 mm in length. Its resistance at the S. B. P. was about 13.1 ohms, the measuring current 0.006 amperes, causing a rise of less than 0°.01 C. in the temperature of the thermometer coil. The potential terminal method of measurement was used (see above reference), permitting changes of less than 0°.02 C. to be detected with certainty.

Using either the cylindrical or conical radiation shield, with umbrella top to eliminate condensation cooling, and taking measurements at various depths of immersion in the vapor, and for all positions within the shields up to 2 cm of the top, no variations as great as 0°.05 C were observed. In the following table, for example, are given the results on two series of measurements for the distribution within the cylindrical shield, the zero position being at the lowest position in the shield corresponding to the bottom of the long resistance thermometers previously used.

| Depth of Immersion of Shield in S Vapor | 0 | 5 | 10 | Distance Thermometer raised in cm |
|---|---|---|---|---|
| 25 cm | 13.128 | 13.127 | $13.128_5$ | Resistance of Therm. |
| 28 cm | 13.126 | 13.126 | 13.127 | Resistance of Therm. |

Outside the radiation shield, of course, the temperature falls off rapidly due to the cooling effect of the liquid running down the tube and to radiation.

Various thermocouples of wire 0.6 mm diameter and which had been subjected to high temperature usage were tried, with results varying from 0°.0 to 1°.0 for the apparent range of temperature within the shield. Even with a differential thermocouple, a distribution differing by several tenths degree was obtained according as one junction or the other was raised. The most uniform distribution was found with couples which had been used the least at high temperatures. Finally, in order to eliminate the effects both of conductivity and of heterogeneity in the wires, we used a couple of which the wires were 0.1 mm diameter and which had been annealed and calibrated once, but not otherwise used. With this very fine and electrically homogeneous thermocouple, most satisfactory results were obtained for the temperature distribution in the shield as shown below for an immersion of 27 cm.

| Distance couple raised in cm | 2 | 4 | 6 | 5 | 7 | 9 | 11 | 3 | 6 | 9 | 5 | etc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Change in temperature °C | +.03 | 0 | 0 | +.01 | +.01 | −.03 | +.04 | +.06 | +.02 | −.04 | +.02 | etc. |

These variations are of the order of the error of measurement and of barometric fluctuations.

It appears to be proved, therefore, by a point to point exploration within the radiation shield of the standard form of S. B. P. apparatus by means of suitable resistance and thermoelectric thermometers and for any position of the shield throughout nearly the whole length of the sulphur vapor column, that the temperature is certainly constant to within 0°.05 and probably within 0°.03 C.

As shown previously,[2] the most probable numerical value of the S. B. P. on the scale of the constant volume nitrogen thermometer, as deduced from all the available data, is $444.7_0$ to within 0°.1 C, with a variation of about 0°.09 per mm Hg change in pressure.

In spite of the complexity of sulphur in its chemical behavior, such as possessing several valences and isomeric forms in the solid and liquid states, the fixity of the temperature of its vapor

[2] Waidner and Burgess, Bulletin Bureau of Standards, **7**, pp. 3–11; 1910.

during boiling appears to be all that could be desired. It would seem that the only phenomenon that could cause this constancy to be questioned would be the existence of two forms of liquid sulphur of slightly different boiling points and one form gradually changing into the other with continued boiling. We have never been able to detect any such progressive change in the boiling point over several hours' time. A further test of the constancy of this temperature is the remarkably close agreement on extrapolation to such high temperatures as the silver and copper points (loc. cit.), using for calibration, sulphur that had been reboiled many and few times.

We may therefore say with a considerable degree of positiveness that the temperature defined by the S. B. P. apparatus may readily be reproduced to within $0^{\circ}.05$ with reasonable care; and as compared with the fixed points, either temperatures of freezing or boiling, given by any of the chemical elements, the S. B. P. is the one the most exactly defined, the most certainly reproducible, and the most constant yet studied.

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