cited, some being less and some more. Of the 60 observations included in these 6 series of results, only 2 deviated from the smooth curve drawn among them by more than 0.001°. Thus it is clear that with adequate practice and care this method may serve very satisfactorily to calibrate a thermometer.

We are indebted to the Carnegie Institution of Washington for generous pecuniary support in this work, which was incidental to a careful research having as its main object the determination of the heat of solution of cadmium in acids. This will soon be reported in full. The experimental work was completed in 1915.

Summary.

In this brief paper, it is shown that a thermometer may be accurately calibrated by successive additions, to a known heat capacity, of heat from electrical energy. The experimentation is essentially like that suitable for the determination of heat capacity where temperature changes are accurately known.

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[CONTRIBUTION FROM CHEMICAL LABORATORY, EDGEWOOD ARSENAL, EDGEWOOD.]

FREEZING-POINT SOLUBILITY CURVE FOR SULFUR AND DICHLORO-ETHYL SULFIDE.[1]

BY J. A. WILKINSON, CHRIST NEILSON AND H. M. WYLDE.

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In the preparation of dichloro-ethyl sulfide or mustard gas by the reaction between ethylene gas and sulfur monochloride according to the equation

$$2C_2H_4 + S_2Cl_2 = (C_2H_4Cl)_2S + S$$

one atom of sulfur is set free for every molecule of mustard gas formed, that is, about 20% of sulfur by weight. When first prepared this sulfur stays in solution, but on standing it may precipitate out in such a way as to form a hard cake in the settling tanks or pipe lines. Later methods of manufacture overcame this difficulty, however.

It was the purpose of this investigation to determine the solubility of sulfur in liquid mustard gas and also the nature of the solid phase which separates out at different temperatures.

Preparation of Materials.

The first experiments were made with a very high grade of roll sulfur without purification. Afterwards pure rhombic, monoclinic and amorphous sulfur were prepared and their solubilities determined.

Rhombic sulfur was prepared by recrystallizing the roll sulfur from carbon disulfide solution.

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[1] Published with the approval of Lt. Col. Amos A. Fries, Chief Chemical Warfare Service, U. S. A.

Monoclinic sulfur was prepared by melting the roll sulfur, allowing the melt to cool until nearly all solid, and then breaking the crust and allowing the remaining liquid to run off. The crust and the liquid were discarded and only the fine needle crystals used. This was kept in an oven at 109° to 110° until used. *Amorphous sulfur* was prepared by melting the roll sulfur and allowing it to run in a fine stream into water. After standing for some time this was dried, ground to a fine powder in mortar, and then extracted repeatedly with carbon disulfide to remove all but the amorphous form. The material was used immediately after driving off the excess of carbon disulfide.

Dichloro-ethylsulfide.—A sample of crude mustard gas, from Edgewood Arsenal, which was quite brown and had a large amount of sulfur dissolved in it, was placed in a bath of ice and salt and frozen. On remelting the mustard gas most of the sulfur remained as a precipitate. The clear amber liquid was poured off from this and fractionally distilled twice under reduced pressure. On the second distillation the part which came over under a pressure of 21 millimeters of mercury at a temperature of 98° to 99° was almost water-white and had a freezing point of 13.82°. This was used in the experiments.

Method.

Mixtures of sulfur and mustard gas were weighed into a large test-tube which was inserted into a larger one and held in position by a rubber stopper. This gave an air space between the two, making the rate of heating and cooling slower and more regular. The inside tube was closed by a rubber stopper with 2 holes for the introduction of the thermometer and stirrer. A 2-liter beaker of water or oil, heated with a Bunsen burner, was used as a temperature control.

The temperature of the bath was raised slowly at the rate of about 2° in 5 minutes and the mixture stirred constantly. The temperature was noted at which the 2 phases became one, and then the system was slowly cooled and the temperature again noted when the second phase appeared. The determination was then repeated, heating and cooling at a slower rate and thus increasing the delicacy of the transition point. This method gave very accurate results for that portion of the curve where 2 liquid layers formed. Where the solid phases separated a different procedure was used. The freezing-point determination method developed by the American University Research Division of the Chemical Warfare Section was used where the solid phase was mustard. Where the solid phase was sulfur the method of plotting time against temperature during the cooling was used.

Where the per cents. of sulfur were below 1% a Beckmann thermometer was used for the determination of the lowering of the freezing point. For all the other determinations a thermometer graduated in single degrees and capable of being read to 0.1° was used.

The mustard gas was placed in the test-tube first and weighed accurately to the third decimal place. The sulfur was weighed on a watch glass and transferred to the test-tube. From these weights the per cents. of the components were calculated. After one determination, a second weight of sulfur was introduced into the apparatus. Each point was checked several times with each quantity weighed and the whole series was checked twice. The results given in the data are averages of many readings.

Solubility of Roll Sulfur.

Table I gives the temperature at which the second phase was formed with the different per cents. of sulfur. Also the nature of the second phase is shown, whether it was solid mustard gas, solid sulfur or a second liquid layer.

TABLE I.—SOLUBILITY OF ROLL SULFUR.

% S.	Temperatures. Nature of the solid phase.		
	Solid mustard. °C.	Solid sulfur. °C.	Liquid phase. °C.
0	13.82	...	...
0.1	13.79	...	...
0.3	13.75	...	...
0.7	13.70	...	...
0.9	13.66	...	...
1.48	...	24.0	...
2.44	...	43.0	...
3.38	...	54.0	...
4.31	...	61.0	...
6.10	...	74.0	...
9.09	...	85.0	...
16.66	...	99.0	...
20.00	...	102.5	...
25.18	...	...	110.0
31.00	...	...	120.0
32.00	...	...	122.0
35.00	...	...	127.0
40.00	...	...	133.5
60.00	...	...	143.0
78.00	...	...	135.0
85.00	...	...	124.0
87.00	...	...	117.5
90.00	...	...	105.0
94.00	...	108.0	...
100.00	...	114.0	...

These results are shown in Figs. 1 and 2, Fig. 1 giving all the data and Fig. 2 being drawn on a larger scale so that it will show the part of the curve below 1% sulfur.

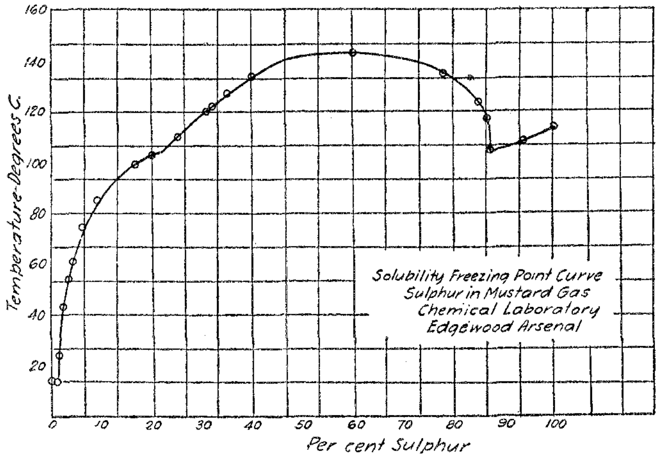

Fig. 1.

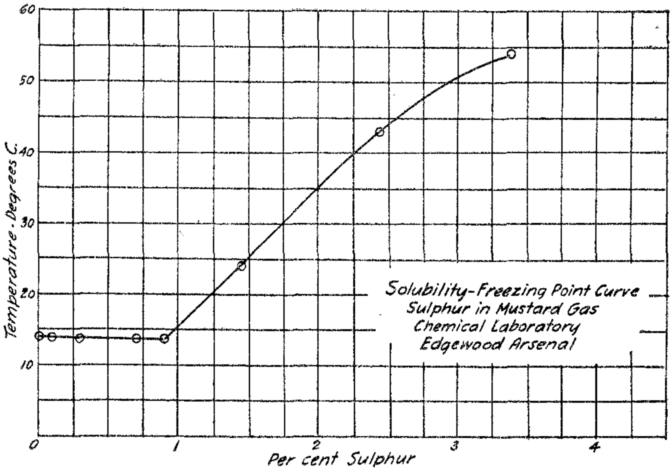

Fig. 2.

Solubility of Rhombic Sulfur.

This determination was made for the purpose of checking the results with those on roll sulfur. Table II gives the data and the comparison with the roll sulfur of the same per cent. composition.

TABLE II.—SOLUBILITY OF RHOMBIC SULFUR.

Rhombic. %.	Temperature. Sol. ° C.	Temperature. Freezing. ° C.	Roll sulfur. %.	Temp. freezing. ° C.
7.6	80	79	7.6	79
11.3	90	90	11.3	90
17.5	100	100	17.5	100
21.0	104	103	21.0	103

These values show that the solubility of the 2 samples of sulfur is the same.

Solubility of Monoclinic Sulfur.

The solubility of monoclinic sulfur was found to agree with that of rhombic. The question then presented itself as to which of the 2 forms was the stable phase in contact with mustard gas at the different temperatures.

On cooling solutions of sulfur in mustard gas until crystals of sulfur separated out, it was found that the nature of the solid phase depended upon the temperature at which it was formed. If above 78° the crystals were monoclinic needles while below that they were rhombic crystals.

These experiments lead to the conclusion that in crystallizing at temperatures below 78° the rate of transformation is too rapid to allow the monoclinic to be stable, while above that temperature we are approaching near enough to the true transition point to make the rate slow enough to allow the monoclinic to form and remain as the solid phase under the liquid.

This is, as would be expected, that the metastable phase or monoclinic crystals would form first and then would change to the stable or rhombic crystals. The rate at which transition would take place would increase the farther one went below the transition temperature (95.5°) until at 78° it would change so rapidly that the presence of the monoclinic form could not be detected. It does not necessarily mean that the transition point of the 2 forms of sulfur is lowered by the presence of the liquid mustard gas.

Solubility of Amorphous Sulfur.

A mixture of 0.14% of amorphous sulfur and 99.86% of mustard gas was heated slowly from 30° to 120°, holding the temperature constant for 10 minutes at every 10° and stirring continuously. There was no evidence of solution of the sulfur until the temperature was raised to 120° at which point the sulfur melted and all went into solution immediately. The solubility of amorphous sulfur is, therefore, less than this amount at temperatures below its melting point.

Conclusions.

(1) The complete solubility curve for sulfur in mustard gas has been determined.

(2) The solubility of rhombic and monoclinic sulfur in mustard gas is the same.

(3) Below 78° the solid phase that crystallizes is rhombic sulfur while above that temperature it is monoclinic sulfur.

(4) The solubility of amorphous sulfur in mustard gas is less than 0.14% at temperatures below 120° at which temperature the sulfur melts.

In conclusion the writers desire to express their appreciation of the helpful suggestions of Major Wm. Lloyd Evans of the Chemical Laboratory of Edgewood Arsenal.

AMES, IOWA.

[CONTRIBUTION FROM CHEMICAL LABORATORY, EDGEWOOD ARSENAL, EDGEWOOD, MD.[

DENSITY AND COEFFICIENT OF EXPANSION OF DICHLORO-ETHYL SULFIDE.[1]

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One of the physical constants of dichloro-ethyl sulfide or mustard gas, which is of great importance in filling gas shells, is the density and the variation of this with changes in temperature. This last is of importance since upon it is based the calculations of the voids necessary to be left in filling the shells in order to prevent the development of leaks. The liquid expanding as the temperature rises completely fills the shells and crushes the threads on the adaptors which hold the boosters.

Since the density at different temperatures was desired, the determinations were made in a dilatometer tube. The same sample could be used to determine the density at the different temperatures and thus the coefficient of expansion could be calculated.

Preparation of Dichloro-ethyl Sulfide.

A sample of mustard gas supposed to be about 97% pure was first distilled by passing the vapor from a constant boiling hydrochloric acid solution through it. The heavier layer of the distillate was then extracted with ether and the ether layer dried over calcium chloride for 12 hours. It was then poured from the calcium chloride into a distilling flask and the ether evaporated off, and the residue distilled *in vacuo,* the middle portion being taken for the density determination. This liquid was almost water-white, having but a very faint yellow tinge. Its freezing point was 13.5°.

Determination of Density.

The stem of the dilatometer was calibrated before sealing to the bulb by weighing the amounts of mercury delivered by the different lengths of the capillary. The volume of the bulb was determined by weighing the dilatometer empty and filled to the zero mark with mercury.

The mustard gas was introduced into the dilatometer through a very fine capillary tube made by drawing out a piece of glass tubing. The dilatometer was immersed in a water bath at 15° and filled with mustard gas adjusting the level to the zero mark after equilibrium had been reached. The top of the dilatometer was then sealed off and it and the contents

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