magnitude of the *additional resistances* (in ohms) depends, at equal working conditions, on the *chemical character* of the electrodes and on the *concentration of hydrogen peroxide.* They are smaller with platinum than with tin electrodes and are at 1000 cycles/sec. about half the value obtained at 50 cycles/sec. For a given hydrogen peroxide concentration ΔR is a constant that must be counted with in conductivity measurements. If the quantities of hydrogen peroxide change during a reaction, the course of which is followed by conductometric measurements, then the ΔR will vary continuously. The temperature coefficient is negative and is about 1% per degree. *The neglect of these changing additional resistances leads to false computations and to thoroughly misleading conclusions.*

JERUSALEM, PALESTINE RECEIVED FEBRUARY 27, 1941

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

The Freezing Point of Phenothiazine*

BY L. E. SMITH AND O. A. NELSON

Most of the investigations into the properties of phenothiazine by workers in the Department of Agriculture and elsewhere have been limited to determinations of its toxicity to various types of insects, its anthelmintic properties, and its value in therapeutics. The melting point of phenothiazine as reported in the literature[1,2] or in chemical handbooks is usually 180–181°. This melting point has been taken as a criterion for the purity of the compound, and it has been common practice to recrystallize phenothiazine until the crystals gave this melting point, when the compound was accepted as pure. In the course of studies made by the authors on the vapor pressures, rates of evaporation, and freezing points of binary mixtures of phenothiazine, it was noted that repeated crystallizations gave crystals of phenothiazine having a melting point significantly higher than that previously recorded. The present study is concerned with the preparation of this compound in pure form and the accurate determination of its freezing point.

Experimental

Purification of Material.—A lot of recrystallized phenothiazine prepared commercially was subjected to repeated recrystallizations from toluene and butanol, decolorizing with norite. In all cases the compound after filtration was dried in an Abderhalden drier, evacuated to 16 mm. at 100°, for five to six hours. Crystallizations were repeated until no increase in melting point or freezing point was observed. A portion of the final recrystallization product was sublimed at 130° at 1 mm. pressure. Part of the resulting sublimate was again recrystallized from toluene.

Freezing-point Apparatus.—The apparatus shown in Fig. 1 is believed to be a decided improvement over the devices commonly used for melting-point and freezing-point determinations. The sample (approximately 1 g.) was

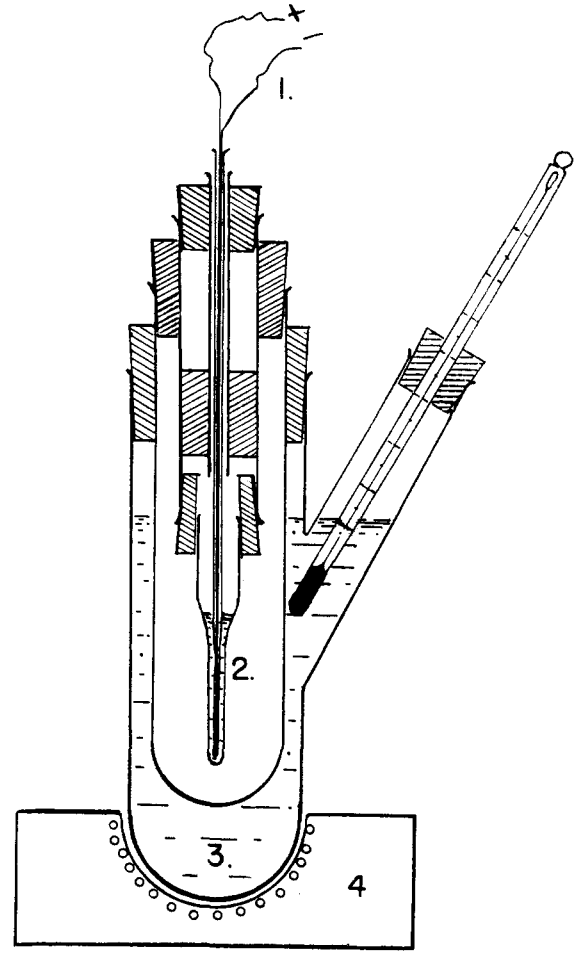

Fig. 1.—Freezing point apparatus: 1, thermocouple; 2, freezing point tube; 3, liquid bath; 4, electric heater.

* Not copyrighted.

(1) Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," second edition, 1931, pp. 325–6.

(2) Richter–Anschütz, "Chemie der Kohlenstoffverbindungen," Dritter Band, 12 Auflage, 1931.

packed into the narrow tube (2), which was suspended in an air-bath. The liquid bath (3) served as an insulator for the air-bath, and also to bring it up to the required temperature. A thermometer suspended in the liquid bath indicated the approximate temperature of the air-bath, while a sensitive thermocouple (1) inserted directly into the sample showed the exact freezing temperature of the phenothiazine. The liquid bath was heated by means of an electric heater (4) connected to a variable-voltage transformer. The thermocouple was made of 34-gage copper and constantan wires, with the hot junction inserted into a 3-mm. glass tube one end of which was drawn down to about 1 mm. and sealed. A drop of mercury in the constricted portion of this glass tube helped to make thermal contact between the hot junction and the surroundings, thus reducing any lag to a minimum. The mercury droplet did not affect the characteristics of the thermocouple. By means of a precision potentiometer and galvanometer, the voltage produced was read to within 1 microvolt—equivalent to 0.019° at the melting point of phenothiazine. The thermocouple, standard cell, and potentiometer were standardized at the National Bureau of Standards previous to their use in this work.

Procedure for Freezing-point Determinations.—After the sample had been packed into the freezing-point tube and the apparatus assembled as shown in Fig. 1, the temperature was raised until the solid phenothiazine had melted. (The approximate melting temperature could also be determined, but since the heat required for melting the sample had to be drawn from the surrounding air the melting point was not so sharp as the freezing point.) The voltage input to the electric heater was then reduced until the temperature of the liquid bath dropped to 3 or 4° below the freezing point of the phenothiazine, and the molten material was allowed to cool. The molten compound was permitted to supercool to 0.1–0.5° below the freezing point, when crystallization was induced by "scratching" or seeding. The temperature then rose to the freezing point where it remained constant during crystallization. During the period of cooling and freezing the molten phenothiazine was stirred by an up-down movement of the glass tube containing the thermocouple.

Results

The highest freezing point obtained for recrystallized phenothiazine was 184.21 ± 0.02°. This freezing point was obtained after three recrystallizations from toluene and butanol. These experiments were replicated four times. One sample of sublimed material followed by two recrystallizations from toluene gave a freezing point of 184.7°.

In seven replications the freezing point determined in our apparatus of sublimed phenothiazine varied between 185.10 and 185.13°. Three replications of melting points gave an average of 185.14 ± 0.04°. The freezing point of pure phenothiazine was thus established at 185.11 ± 0.02°.

From the results obtained in this investigation it is evident that to obtain phenothiazine of the highest purity the compound must be sublimed under carefully controlled conditions. This is demonstrated by the fact that when phenothiazine is recrystallized after sublimation the product has a significantly lower freezing point, and also that repeated recrystallizations of the original material did not raise the freezing point of the crystals obtained above 184.21 ± 0.02°, or approximately 0.9° lower than that of the pure compound.

Summary

The freezing point of pure phenothiazine prepared by sublimation has been found to be 185.11 ± 0.02°.

BELTSVILLE, MD. RECEIVED SEPTEMBER 29, 1941

NOTES

The Disproportionation of R_6Pb_2 Compounds

BY GEORGE CALINGAERT, HAROLD SOROOS AND HYMAN SHAPIRO

It was shown in a previous paper from this Laboratory[1] that the different alkyl groups in mixtures of R_4Pb compounds will, under the influence of a suitable catalyst, redistribute themselves at random between all the lead atoms, giving a mixture of all the possible R_4Pb compounds in which the concentration of each of these compounds can be predicted on the basis of the probability law. R_6Pb_2 compounds, on the other hand, when heated, disproportionate to yield the corresponding R_4Pb compounds and metallic lead, and it has been suggested[2] that this takes place in accordance with the equation

$$2R_6Pb_2 = 3R_4Pb + Pb \qquad (1)$$

The question then arises as to whether the decomposition of a mixture of R_6Pb_2 and R'_6Pb_2 will yield only R_4Pb and R'_4Pb, or whether it will

(1) Calingaert, Beatty and Soroos, THIS JOURNAL, **62**, 1099 (1940).

(2) Calingaert, *Chem. Rev.*, **2**, 43–85 (1925).