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AN APPARATUS FOR THE DETERMINATION OF MELTING POINTS

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A comprehensive summary of methods and devices for the determination of the melting points of organic substances is given in Oesper's translation of Lassar-Cohn's "Organic Laboratory Methods," with notes and comments by Roger Adams. None of the methods there described is rapid, several of them are of doubtful accuracy, and all of them, with perhaps the exception of the Maquenne block, fail to give correct results if the substance tends to decompose before it reaches the melting point.

One of the most accurate and rapid methods for the measurement of temperature is by a thermocouple used in conjunction with a potentiometer. An apparatus that employs this combination, and with which the melting points of substances, either organic or inorganic, within the range from room temperature to 300°, may accurately be determined in a few seconds, is shown in Fig. 1. A is a bar of very pure[1] copper 61 cm. long. It is

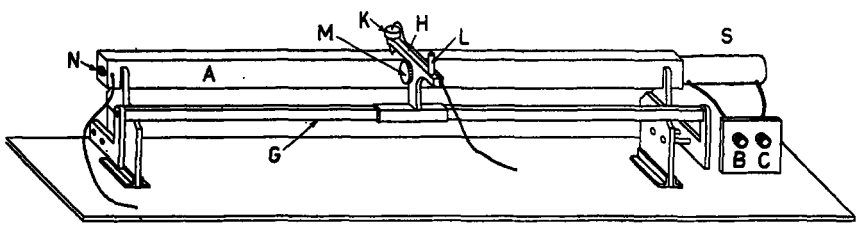

Fig. 1.

square, 25 mm. × 25 mm., through about 53 cm. of its length and the remaining 8 cm. is turned down to a cylindrical shoulder 2 cm. in diameter. This shoulder, S, is first covered with a thin layer of asbestos paper, and then 18 turns of nichrome ribbon, $^1/_{16}$ in. × 0.0325 mm., are wrapped around it. The ends of the ribbon are fastened to the two binding posts B and C. The coil of ribbon is covered with a layer of asbestos cement about 6 mm. thick. A current, either a. c. or d. c., passed through this ribbon, heats the bar A, and is so adjusted by suitable resistance that the range of temperature of the bar between the hotter and cooler ends includes the temperatures of the melting points of the substances under examination.

Parallel with the copper bar A is a guide rod G that carries the pivoted arm H to which is fastened an insulated wire of constantan. The end

[1] Spectroscopic examination showed that it contained only minute traces of aluminum, magnesium and iron.

of this wire passes through the head K of the arm, and the exposed end of the wire is lightly but firmly pressed down upon the surface of A by a spiral spring in L when the button M is turned to the left. The arm is raised from the bar and held there, by turning the button M to the right.[2]

Copper and constantan were employed as the thermoelectric pair because in respect to thermoelectric power, homogeneity and permanence,[3] this couple is admirably adapted to measurements between room temperature and 400°. The constantan wire that was used is No. 20, diameter 0.08 mm.

The further end of the constantan wire, and a pure copper wire, 0.08 mm. in diameter, which is fastened to the cooler end of A by the binding post N, are connected to a potentiometer.[4] No calibration of the heated bar A is necessary. It need only be brought at some point (any point) to the temperature at which the substance under examination will melt. The differences of temperature between the two ends of A were found to be as follows:

Current through heating coil around S, amp.	Hotter end,[5] °C.	Cooler end, °C.
4	90	63
5	131	87
6	140	95
7	176	107
8	233	131
9	250	150
10	302	167

A determination of the melting point of a substance is made as follows. When the bar A has been brought to such a temperature that somewhere (anywhere) along its length the melting point of the substance under

[2] To ensure satisfactory construction of the apparatus, application for a patent on the device has been made.

[3] See White, THIS JOURNAL, **36**, 1856, 1868, 2011, 2480 (1914).

[4] The potentiometer was a double-range potentiometer indicator of the Leeds and Northrup Co., scales 0–16 millivolts, and 0–80 millivolts, their catalog No. 8657-B. This instrument is equipped with a manual cold junction compensator that is set by means of a dial to the millivolts corresponding to the temperature, as read from a thermometer, of the cold junction of the thermocouple that is being employed. With a potentiometer not fitted with such a compensator the cold junction of the thermocouple must be maintained at 0°.

[5] Melting points as high as 320° have been determined with the bar, but it is not advisable to hold the bar at a temperature above 275° for any considerable length of time because superficial oxidation of the copper may result. The thin layer of oxide does not, however, appreciably affect the determination, if the constantan contact is firmly pressed down with the finger. The bar can easily be cleaned with a "metal polish," several satisfactory kinds of which are on the market. Bars of metals other than copper, for use with substances of melting points above 300°, are now being tested.

examination is reached, particles of the finely-ground substance are dropped along the surface of the bar from a small spatula or knife blade. The arm H, with the point of the constantan wire raised, is slid along the guide rod, and by turning the button M the end of the constantan wire is brought down upon the bar exactly on the line separating the melted from the unmelted substance. This line is a very sharp one. The potentiometer is then read, and the temperature corresponding to the observed current is taken from the standard calibration tables.[6] With this apparatus readings can be made that are accurate within 10 microvolts = 0.25°.

The arm H is then raised by turning M, the surface of the bar A is wiped off with a clean cloth, and the apparatus is ready for the next determination. The whole manual operation need not take longer than thirty seconds, and the operation is so rapid that accurate results are obtained even when the substance dissociates upon brief heating.

Uniformity of Results with Bar A at Different Temperatures.—The melting point of acetanilide was determined at different points along the bar with the hotter end of the bar held at four different temperatures, 125, 150, 180 and 200°. The observed melting point was the same (114.25°) in all cases.

TABLE I

DETERMINATIONS OF MELTING POINTS OF VARIOUS COMPOUNDS WITH ELECTRIC BAR

Organic Compounds

	Literature		Found
Benzophenone		48.5	48.2
p-Nitrotoluene	51.3	51.5	51.5
Palmitic acid	63	64.0	64.1
p-Bromo-aniline	66.0	66.4	66.5
Stearic acid	69.0	66.4	69.8
o-Nitro-aniline	71.0	71.5	71.6
Naphthalene	80.0	80.1	80.2
Triphenylmethane	92	92.5	92.5
Acetanilide	114.0	114.2	114.25
Mandelic acid	117.8 118	118.2	118.5
Benzoic acid	121.1	121.0	121.1
p-Bromonitrobenzene	66	66.4	66.5
Urea	132.2	132.7	132.8
Cinnamic acid		133.0	133.2
m-Nitrobenzoic acid	140 141.4	141.6	141.6
p-Bromo-acetanilide	165.4 167	168.0	166.0
Hippuric acid	187.0	187.5	187.3
p-Hydroxybenzoic acid		213.0	213.2
Caffeine		234.0	234.4

[6] Bulletin No. **170**, Bureau of Standards, "Pyrometric Practice," p. 309. Also in "International Critical Tables," **1926**, Vol. I, p. 58.

TABLE I (*Concluded*)

			Literature	Found
Metallo-organic Compounds				
Diphenyl mercury	120	121.8	124.5	124.6
o-Nitrophenyl mercuric chloride			182.0	182.0
α-Naphthyl mercuric chloride	188–189		188	188.9
Ethyl mercuric chloride			192.5	192.7
Inorganic Compounds				
Ammonium nitrate			169.6	169.6
Silver nitrate		209	212	211.4

Determination of Melting Points of Substances that Readily Dissociate or Sublime when Heated.—In the tabulation of melting points of organic substances in the "International Critical Tables," Vol. I, pp. 176–275, the value for many compounds is followed by a "d," meaning that the substance decomposes when being heated to determine its melting point by the method that was employed. These values cannot, of course, be regarded as the correct melting points of the compounds. When determined by the "capillary tube" method, the apparent melting point of a substance that decomposes when being heated may vary between wide limits, the variation depending upon the procedure employed. The rate of heating is one of the chief causes of these differences. Some substances of this character were tested with the apparatus here described, and in every case definite melting points were obtained, and several determinations of each were practically identical.

TABLE II

MELTING POINTS OF SOME SUBSTANCES THAT READILY DECOMPOSE WHEN HEATED

Substance	"Int. Crit. Tables," °C.	Electric bar,[7] °C.
Phthalic acid	191 d.	228.5
Alloxan	170 d.	210
Barbituric acid	240 d.	250
Glycine	232 d.	297.2
Fumaric acid	287 d.	297

The melting point of phenyl boric acid is given by Pace[8] as 204°. Recent determinations in the Cornell Laboratory by the "capillary tube" method gave 210–212°. Inasmuch as the anhydride of the acid is formed when the acid is heated, the melting points were those of mixtures of the anhydride and the acid. With the electric bar several determinations of phenyl boric acid agreed exactly at 222.5°.

Speed of Determinations of Melting Points by Different Methods.—In these determinations the melting points were not known to the operator.

[7] The compounds were not of high purity; the results are therefore merely illustrative of the applicability of the method to such cases, and are not to be regarded as the correct melting points.

[8] Pace, *Atti accad. Lincei*, **10**, 193 (1929).

If they had been, the determinations with the capillary tube and Maquenne block might have taken appreciably less time.

TABLE III

SPEED OF DETERMINATIONS OF MELTING POINTS BY DIFFERENT METHODS

Substance	I	II	III	IV	Time for the 4 detns.
Capillary tube method	118.5	121	167	91	1 hour
Maquenne block	118.5–119	120.5	166–167	91–92	4 hours[a]
Electric block	118.5	121.1	166	92.5	2 minutes
M. p. in literature	118.5	121.1	165.4	92.5	

[a] Because of difficulty in controlling the temperature of the bar.

Summary

This article describes a device for the measurement of the melting points of substances, particularly of organic substances, up to temperatures of about 300°. With the apparatus, melting points can be determined in about thirty seconds with an accuracy of about 0.25°.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A CONTRIBUTION TO THE STUDY OF CHAIN REACTIONS. (A) REMARKS ON A PAPER BY LENHER AND ROLLEFSON ON THE KINEMATICS OF PHOSGENE. (B) THE MECHANISM OF THE FORMATION AND DECOMPOSITION OF ETHYLENE IODIDE

BY HANS JOACHIM SCHUMACHER[1]

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Introduction

Recently a paper by Polissar[2] on the kinetics of the thermal decomposition of ethylene iodide appeared in THIS JOURNAL. The decomposition was carried out in the presence of iodine in carbon tetrachloride solution. The interesting result of this careful investigation is that the velocity of the decomposition can be represented by the equation

$$-\frac{d[C_2H_4I_2]}{dt} = k[C_2H_4I_2][I_2]^{1/2}$$

This equation is, as mentioned by Polissar, similar to that of the phosgene decomposition, which is given below

$$-\frac{d[COCl_2]}{dt} = k[COCl_2][Cl_2]^{1/2}$$

Polissar, in his discussion of results, seems to have misunderstood the mechanism of the phosgene decomposition and his interpretation of the

[1] International Research Fellow.

[2] M. J. Polissar, THIS JOURNAL, **52**, 956 (1930).