form is obtained by precipitation of a cold alkaline solution with acetic acid and is believed to have a lactoid structure. The *red* form is obtained by precipitation of a boiling alkaline solution with acids and is believed to have a *p*-quinoid structure.

2. No other forms of fluorescein were obtained than the yellow lactoid form and the red quinoid form; von Liebig's claims to the existence of five different yellow forms must be in error.
3. The yellow lactoid fluorescein and the red quinoid fluorescein give different yellow hydrochlorides.
4. The colorless diacetate, bisphenyl carbamate and hydrazide of fluorescein have been prepared. These are derivatives of lactoid fluorescein.
5. The red mono-ammonium salt and the red methyl ester and its orange acetate have been prepared. These are derivatives of quinoid fluorescein.
6. Dibromofluorescein, its hydrochloride and diammonium salt have been prepared. These colored compounds are derivatives of quinoid fluorescein.
7. Dibromofluorescein dibenzoate has been prepared. This is colorless and a derivative of lactoid fluorescein.
8. Colorless eosin has been prepared. The introduction of bromine has made the lactoid form stable and colorless.
9. Two colored hydrates of eosin have been prepared.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE MARTIN MALONEY CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY OF AMERICA]

THE VAPOR-PRESSURE CURVE OF BENZOIC ACID

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Introduction

The determination of the vapor pressure of benzoic acid from 100 to 180° was suggested by Zanetti.[1] The authors did not limit themselves to this range, but have determined values from 50 to 250°. As two different methods were used, one for each phase, this paper is divided into two parts for convenience.

I.[2] The Vapor Pressure of Benzoic Acid (Liquid) from 251 to 128.6°

The vapor pressure of liquid benzoic acid has already been determined by Kahlbaum.[3] He used a static method and his results are very accurate

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[1] Zanetti, *Ind. Eng. Chem.*, **16**, 304 (1924).

[2] Extract from a thesis submitted in partial fulfilment of the requirements for the degree of Master of Arts, by Robert J. Flanigan.

[3] Kahlbaum, *Z. physik. Chem.*, **26**, 603 (1898).

and consistent except at the lower temperatures near the melting point, 121.7°.[4] In the redetermination of these values we have used the isoteniscope of Menzies.[5] The only unknown factor in the method, provided constant temperature is maintained, is the reading of the manometer, which can be done with the aid of a cathetometer.

Materials

The benzoic acid used was Bureau of Standards Sample No. 39b, which is employed as a standard in calorimetry and acidimetry.

The mercury used in the gage and seals was washed, dried and redistilled under a low pressure.

All thermometers were compared against standards and checked at the ice point and boiling point.

The manometer was a Pyrex tube 6 mm. in diameter and 1.5 meters long, filled with the cleaned mercury and boiled out under an extremely low pressure, obtained with the aid of a Hyvac pump, and then sealed off.

Results

Several series of determinations were made. The best of these can be represented by the curve $\log P_v = 30.172 - 4714\,(1/T) - 6.720\,(\log T)$, where T represents absolute temperature.

The general agreement of the points with this equation is shown in Table I.

TABLE I

LIQUID BENZOIC ACID

t, °C.	P, obs.	P, calcd.	Deviation, %
128.6	8.4	8.6	−2.3
134.5	11.8	11.6	1.7
148.0	22.2	21.9	1.4
158.2	34.0	34.3	−0.9
172.8	63.8	63.0	1.3
187.6	110.8	110.9	−0.1
199.7	166.8	167.7	−0.5
216.2	286.7	290.4	−1.3
233.0	478.8	482.0	−0.7
247.0	718.1	709.6	1.3

Discussion of Results

The results as a whole are fairly consistent and fall on either side of the curve. They also agree well with those of Kahlbaum, which only deviate from our equation on an average of 1%, except below 132°, where this deviation is 5%.

[4] "International Critical Tables," McGraw-Hill Book Co., New York, **1926**, p. 208.

[5] Smith and Menzies, THIS JOURNAL, **32**, 1419 (1910).

II

Vapor Pressure of Benzoic Acid (Solid) from 50 to 121°

The vapor pressure of solid benzoic acid has also been determined from 60 to 110° by a dynamic method.[6] Although Niederschulte's results are fair, they are not consistent and could not be used to extrapolate to the melting point, as the slope was uncertain.

The authors have employed the static method of Menzies,[7] which turned out to be more difficult to operate, but is capable of giving results with a high degree of accuracy.

Apparatus

A glass bulb of 733 cc. capacity, containing the solid benzoic acid, was suspended in an oil-bath whose temperature was controlled by a regulator to 0.1°. This bulb was sealed through a trap to two McLeod gages, which in turn were connected to a Hyvac pump through a mercury seal. A vacuum stopcock was also included to admit nitrogen dried over phosphorus pentoxide.

The McLeod gages were made of capillary tubing, calibrated by the Bureau of Standards. The capillary tubing was 20 cm. long and contained 1 cc. The volumes of the bulbs were measured by filling with mercury and weighing. They were 139.2 cc. and 10.94 cc., respectively.

The volume of the bulb which held the acid was determined by filling with water and measuring in a graduate.

The volume of the system was calculated by admitting a known volume of air and observing the increase in pressure. This method gave from two determinations results which only differed by one part in 1500.

Manipulation

A measurement was made by evacuating the system and washing it out with dry nitrogen. A reading of the pressure (P_1) at room temperature (T_1) was taken; the temperature of the bath was raised to T_2 and another reading of the pressure (P_2) made and all were noted. These second observations were repeated until they became constant. P_1 and T_1 are called the zero reading.

Calculations

Although Menzies says:[7b] ". . .an obvious application of the gas laws enables one to compute the vapor pressure of the substance at the final temperature, provided in particular, that Dalton's law may be assumed," no formula is given. With the aid of these assumptions we have derived the following formula, where V_s and V_b represent the volumes of the system and bulb, respectively: $P_v = P_2 - P_1(T_2/T_1) + V_s/V_b(P_2 - P_1)T_2T_1$.

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[6] Niederschulte, *Dissertation*, Erlangen, **1903**.

[7] Menzies, (a) THIS JOURNAL, **41**, 1783 (1919); (b) **42**, 2218 (1920).

Results on the Vapor Pressure of the Solid

Several determinations were made on the solid, using various initial pressures. The vapor pressure was then calculated by the Menzies formula and found to be on a straight line which is represented by the equation log $P_v = 11.956 - 4409\ (1/T)$.

Table II shows the deviation of some of the points from this line.

TABLE II

SOLID BENZOIC ACID

t, °C.	P, obs.	P, calcd.	Deviation, %
60.1	0.0527	0.0525	0.13
80.4	.308	.0303	.15
100.2	1.436	1.400	2.5
121.0	5.830	5.807	0.3
	Deviation of Niederschulte's points		
60	0.11	0.052	110
75.4	.19	.200	65
96	.91	1.014	−10
110	3.74	2.992	24

Discussion of Results

Several points should be noted about the results on the solid: (1) the very consistent agreement of all our values; (2) the difference in slopes of the two curves gives a latent heat of fusion for benzoic acid as 32.8 cal., a value in good agreement with that of Mathews, namely, 34.8 cal./g.[8] and that of Garelli and Montanari, 39.65 cal./g.[9]

More than 200 observations were made on the solid, but only those of final runs whose values are consistent were used to determine the curve.

Two causes of error may occur: (1) the failure to wait long enough for the system to reach equilibrium, which yields values that are too low; (2) adsorption of gases in the bulb, causing a more serious error. The first run, especially at low pressure, is never reliable for this reason, and only a zero reading checked after a run leads to any consistent values.

As mentioned by Menzies, the ideal condition (for accuracy) is a pressure of nitrogen slightly greater than the vapor pressure to be measured. But if it is too close, rapid sublimation results with the blocking of the tube.

This method should find wider application in the measurement of vapor pressures of solids, as it is more accurate and faster than the loss-in-weight air-bubbling method, and makes no assumption as to the molecular weight of the vapor.

Summary

The vapor pressure of benzoic acid has been measured from 250 to 50°.

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[8] Mathews, THIS JOURNAL, **39**, 1125 (1917).

[9] Garelli and Montanari, *Gazz. chim. ital.*, **24** [2], 229 (1894).

The values above 130° have been found to be in agreement with those of Kahlbaum. Two of the four values of Niederschulte lie near the vapor-pressure curve of the solid, as determined by us.

The latent heat of fusion as calculated from the difference in slopes of the two curves is in agreement with cryoscopic data.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

PYROGALLOLBENZEIN AND SOME OF ITS DERIVATIVES

BY W. R. ORNDORFF AND CHEN WANG[1]

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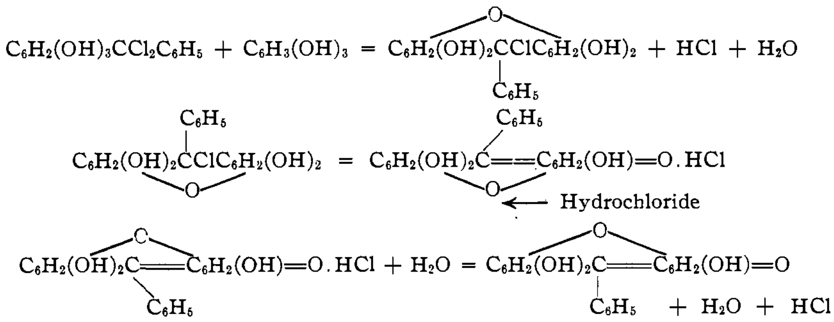
The method of preparation, purification and the analyses of pyrogallolbenzein have already been given.[2] The red aqueous extracts obtained in the purification of the benzein[2] were concentrated and on cooling gave red crystals. Yellow crystals were obtained when these were crystallized from water, after boiling the solution with bone black. Analyses[3] showed that this substance was 2,3,4-trihydroxydiphenyl ketone, known commercially as Alizarin Yellow A. The triacetate, sodium and lead salts were also made and analyzed[3] and proved that this by-product obtained in the preparation of the benzein was 2,3,4-trihydroxydiphenyl ketone. The pyrogallol probably first reacts with the benzotrichloride to form trihydroxydiphenyldichloromethane, $C_6H_3(OH)_3 + C_6H_5CCl_3 = C_6H_2(OH)_3CCl_2C_6H_5 + HCl$, and this, on boiling with water, gives 2,3,4-trihydroxydiphenyl ketone, $C_6H_2(OH)_3CCl_2C_6H_5 + H_2O = C_6H_2(OH)_3COC_6H_5 + 2HCl$. The formation of the pyrogallolbenzein itself probably takes place as follows.



$$C_6H_2(OH)_3CCl_2C_6H_5 + C_6H_3(OH)_3 = \overbrace{C_6H_2(OH)_2\underset{C_6H_5}{\underset{|}{C}}ClC_6H_2(OH)_2}^{O} + HCl + H_2O$$

$$\underbrace{C_6H_2(OH)_2\overset{C_6H_5}{\overset{|}{C}}ClC_6H_2(OH)_2}_{O} = \underbrace{C_6H_2(OH)_2\overset{C_6H_5}{\overset{/}{C}}{=\!=}C_6H_2(OH){=}O}_{O}.HCl$$

$\leftarrow$ Hydrochloride

$$\overbrace{C_6H_2(OH)_2\underset{C_6H_5}{\underset{\backslash}{C}}{=\!=}C_6H_2(OH){=}O}^{C}.HCl + H_2O = \overbrace{C_6H_2(OH)_2\underset{C_6H_5}{\underset{|}{C}}{=\!=}C_6H_2(OH){=}O}^{O} + H_2O + HCl$$

Pyrogallolbenzein

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[1] From a dissertation submitted by Chen Wang to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Orndorff and Wang, THIS JOURNAL, **47**, 290 (1925).

[3] See *Thesis*, Cornell University Library. International atomic weights for 1925 were used in all calculations.